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A STUDY OF GALVANIC CORROSION IN MARINE PSEUDO-SEDIMENTS

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Research Conducted through the

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by

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Dale F. Leipper, Project Supervisor

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ABSTRACT

Corrosion tests are described in which mono-metallic couples are exposed as concentration cells in pseudo-marine environments. Data on S.A.E. 1020 steel and aluminum alloy Al Cl S - T6 are presented. The natural system which the cells simulate, is one in which a single piece of metal is exposed through the interface between marine sediments and the overlying sea water. Effects of marine sulfate-reducing bacteria are superimposed over the physico-chemical system. The polarities of the cells studied, as well as data relating cell resistance to galvanic current, are presented. Possible effects of redox potential (E_h) and pH are discussed. The data presented show that the strain of marine sulfate-reducers used in these experiments causes a change in the cathode compartments, of cells containing mild steel electrodes in nutrient medium, which results in as much as a 200 fold increase in galvanic current. The study of potential-time data and polarization phenomena indicate that cathodic depolarization is involved.

INTRODUCTION

The sulfate-reducing bacterium, Desulfovibrio desulfuricans,[1] has long been known to accelerate the corrosion of iron under anaerobic conditions but the mechanism of this reaction has been subject to controversy. Both cathodic and anodic polarization effects, as well as the medium supporting the culture, have been considered responsible for the reaction of the metallic surfaces involved. In general, two methods of study have been used. One was based on the stoichiometric relationship between the weight loss of iron electrodes and the quantity of sulfate ion reduced and the other on the study of potential-time curves. In the work described in this paper, galvanic cells were constructed in which the electrodes were as nearly identical as possible while anolyte and catholyte differed. In this manner the direction of current flow was determined by the reactions of the half-cell electrodes to their electrolytes and the effects of sulfate-reducing bacteria were studied as they were superimposed over a pre-existing polarity. Aluminum alloy 61-S [2] and S. A. E. 1020 steel,[3] because of their different polarization characteristics, were used in the experiments described.

LITERATURE SURVEY

A. The Environment of Anaerobic Corrosion

The literature contains many references to the influence of sulfate-reducing bacteria on the corrosion of steel. Papers on corrosion by marine sulfate-reducers typically dealt with local cell action or with the anaerobic corrosion associated with fouling. Some attention has also been given to corrosion rates of steel exposed through the interface between sulfide-rich marine sediments and the overlying water. In the literature examined, the most exhaustive studies were carried out by Starkey and Schenone(26) who stated that the highest corrosion rates of steel occurred at the mud line. It was also stated that steel specimens buried completely in low redox potential sediments often showed lower weight losses than similar specimens exposed through the sediment-water interface. Considerable emphasis was placed upon sulfate-reducing bacteria as agents promoting corrosion but the electrochemical approach to the problem was not used. The paper was quantitative only inasmuch as weight loss data and micrometric measurements were presented.

Little quantitative work has been done on anaerobic corrosion by marine sulfate-reducers and the author has depended much upon analogies drawn from work on fresh water and soil corrosion of this type. In his review article, Deuber (4) has outlined the important aspects of the microbiological corrosion problem and presented a bibliography of considerable scope. An excellent

[1] Also listed under the genera Vibrio, Sporovibrio, Microspira and Spirillum. The accepted generic name for sulfate-reducers is now Desulfovibrio. Some literature refers to the halophilic strain as D. estuarii but the distinction is no longer made in this country.

[2] Supplied by The Aluminum Company of America

[3] Supplied by The United States Steel Company

review of the literature and a summary of the cathodic depolarization theory of anaerobic corrosion was given by von Wolzogen Kühr and van der Vlugt (31). These authors stated that residual stresses left in iron water pipes after fabrication resulted in galvanic micro-cells, the cathodic members of which were subject to depolarization by hydrogen-utilizing bacteria, aerobic or anaerobic. They pointed out that the anaerobic environment required by sulfate-reducers was established through the utilization of oxygen by aerobic species of oxyhydrogen and iron bacteria. The ultimate result of this mechanism was tubercle formation and localized corrosion on the internal walls of water mains. Starkey and Wight (25), Pont (16), and Bunker (2,3) have reported on corrosion in anaerobic soils. Reducing conditions and the presence of sulfate-reducing bacteria were found to correlate well with the occurrence of highly corrosive soils.

It has been reported that the redox potential and oxygen concentration in marine sediments are associated with the distribution of bacteria (39). Sediments, due to oxygen utilization by aerobic organisms, are known to have lower redox potentials and oxygen concentrations than the overlying sea water. However, the oxygen concentration just above the mud line is known to be quite low. This could result in inefficient depolarization of cathodic areas on metallic objects exposed through the sediment-water interface. The metabolic activity of sulfate-reducing bacteria in the anaerobic sediments could depolarize cathodic areas on the portion of the metallic structure extending below the mud line, and the reducing capacity of the sediments should tend to stifle oxidation reactions. In Evans description of the classical differential aeration cell (6), the aerated electrode was cathodic to the air-free electrode but only because oxygen is a cathodic depolarizer. Thus, with a poorly aerated stratum of sea water and a more efficient cathodic depolarizer in the anaerobic sediments, there would be no reason to insist that the cathode in such a cell must be the aerated electrode. La Que (13) has stated that the corrosion rate of steel in sea water is controlled by cathodic depolarization. This author has also suggested that the high weight losses encountered at the mud line may be due to abrasion by particles carried in bottom drift or a "peculiar effect of sulfate-reducing bacteria"(12). The mechanism of cathodic depolarization by sulfate-reducers, acting through the sediment-water interface, could be responsible for the weight losses observed.

In the work of ZoBell and Rittenberg (41), it was shown that sulfate-reducing bacteria prefer loosely compacted sediments containing large amounts of sand to tightly compacted clay sediments. Deuber (4) and Bunker (2,3) apparently with reference to non-marine environments, stated that poorly drained clay soils containing organic residues are most likely to support the anaerobic corrosion mechanism. The terminology here is only relative and it is felt that a terrestrial soil considered to be of high clay content might be considered coarse in many marine environments. Whitehouse (37) reported that the most predominant clay type of inland bays and immediately off-shore regions of the Texas Gulf Coast is montmorillonite and that in certain areas this clay comprises the major component of the sediments. For this reason, bentonite, largely montmorillonitic in composition, was used in some of the experimental exposures described. The reader is referred to the discussions of Grim (8), Mason (15) and Whitehouse for the structure and chemistry of this clay. It should be noted here that bentonite is probably a sub-optimum culture environment for sulfate-reducing bacteria.

In discussing this work with Dr. C. E. ZoBell of Scripps Institute of Oceanography, the author learned that the term "sulfate-reducer" is extremely ambiguous and that in many cases the greatest similarity between species or strains of bacteria, now lumped under the genus Desulfovibrio, is the ability to reduce one or more states of oxidized sulfur in artificial media. In ZoBell's work, the only cultures considered pure are those grown from single cell isolations. It is quite possible to isolate from a single mud grab several strains with the ability to reduce sulfates but with a limited number of other physiological capabilities in common. Thus, it would seem imperative that the same strain of sulfate-reducer be employed before results of different workers can be compared. In field testing it is impossible to meet this demand and it it probably unnecessary assuming that mixtures of strains result in an average physiological response from one location to another. The sulfate-reducer used in this research was provided by the Division of Microbiology of the Scripps Institute of Oceanography. It is a hydrogen-utilizing heterotroph isolated from the estuarine sediments of Mission Bay, California. In ZoBell's laboratory it is stock culture No. 354.

B. Biochemistry of Sulfate Reduction

Sisler and ZoBell (22) have quantitatively studied the utilization of hydrogen by marine sulfate-reducing bacteria. Both autotrophic and heterotrophic forms have been isolated from marine sediments and studied (21,22,40). Thirty-three of thirty-nine pure cultures isolated were capable of utilizing hydrogen gas. Only three cultures were incapable of utilizing hydrogen autotrophically. The enzyme considered responsible for this biochemical mechanism is termed hydrogenase and is capable of activating molecular hydrogen. von Wolzogen Kühr and van der Vlugt (31) stated that molecular hydrogen must be changed to atomic hydrogen before it can enter into biochemical mechanisms involving sulfate reduction. Kluyver and Manten (11) further stated that an enzyme other than the usual substrate hydrogenase must be responsible for this activation. von Wolzogen Kühr and van der Vlugt considered this enzymatic selectivity responsible for the different growth rates of aerobic hydrogen utilizers when grown in natural water overlayered with oxyhydrogen gas and the same system containing metal specimens. It was reasoned that atomic hydrogen adsorbed on cathodic areas of the metal specimens made possible the omission of one biochemical mechanism, resulting in the growth response observed. A growth lag period was observed in systems from which metallic specimens had been excluded.

Stephenson and Stickland (27,28) demonstrated hydrogenase activity in sulfate-reducing bacteria as well as other organisms. Aerobic bacteria with this physiological capability were found able to reduce oxygen, nitrate, fumarate and methylene blue. Evidence was stated for the probable involvement of the same enzyme in sulfate-reduction by Desulfovibrio desulfuricans. In later research (29), these workers demonstrated the production of methane by single cell isolations of sulfate-reducers. In these studies, Stephenson and Stickland noted that only single carbon compounds were reduced. These were carbon dioxide, formate (as the calcium salt), carbon monoxide, methyl alcohol and formaldehyde, the latter being added as the weakly dissociated compound hexamethylenetetramine. In the formate studies, it was shown that formic acid was first broken down to H_2 and CO_2 by the enzyme formic hydrogenlyase and these products were recombined as methane through the biocatalytic influences of hydrogenase. Sisler and ZoBell (23) have shown that

several strains of marine sulfate-reducers are capable of reducing nitrogen. Nitrogen fixation may be associated with hydrogenase activity. Hoberman and Rittenberg (10), and Lascelles and Still (14) suggested that hydrogenase may be an enzyme of the iron porphyrin type.

Postage (19) has shown that the sulfate-reducing bacteria are capable of reducing a number of the oxidized forms of sulfur including sulfate, thiosulfate sulfite, tetrathionate, metabisulfite, and dithionite. Of further interest were the observations of Postgate (18) concerning an unknown growth factor for these organisms in yeast extract and peptones. Both the individual and synergistic effects of several amino acids were studied in Postgate's work but none of the mixtures employed were capable of reproducing the growth level attained through the use of peptones and yeast extract. It was stated that the missing factor or factors might be of the polypeptide group. Casein hydrolysates were also active in growth promotion, and Sprince and Woolley (24) have shown that strepogenin, isolated from the polypeptides of casein hydrolysates, is active in growth promotion of certain lactic acid bacteria. In Postgate's work, one of the more responsive strains to yeast extract-peptone media was a halophilic strain, Texas 29.12.B, supplied by ZoBell and presumably of marine origin.

Postgate (17) and Rogers (20) have worked on inhibition mechanisms concerning sulfate-reducers. Postgate's work indicated that selenate competitively inhibits the reduction of sulfate, and Rogers has achieved inhibition of growth by the use of proflavine and acriflavine dyes. It was interesting to note the structural similarities between these dyes (35) and riboflavin (36). Both the adenine dinucleotide and the phosphate of riboflavin are prosthetic groups for enzymatic reactions involving hydrogen transfer in biological tissues. It is possible that the dyes used by Rogers in his investigations were anti-enzymatic in nature. The biochemical approach bears much promise for the ultimate control of anaerobic microbiological corrosion.

C. Electrochemical Investigations

Before the results of biochemical investigations can be applied to the control of corrosion by sulfate-reducers, the electrochemical mechanism should be better understood. Wormwell and Farrer (38), Wanklyn and Spruit (32) and Hadley (9) have reported that the potentials of iron electrodes change in the anodic direction when nutrient media in which they are exposed are inoculated with pure cultures of sulfate-reducers. Wanklyn and Spruit found little difference in the corrosion potentials of iron electrodes in sterile autotrophic media and those inoculated with sulfate-reducers. They interpreted the greater negativity of the iron electrode in inoculated heterotrophic media as being due to the production of sulfide occasioned by the addition of the organic hydrogen donor, lactate. This would agree with the concept of sulfide ion as an anodic stimulator. Hadley interpreted this potential change as being due to cathodic depolarization. Wanklyn and Spruit disagreed with this interpretation, stating that cathodic depolarization would be expected to render an electrode more cathodic. The work of von Wolzogen Kuhr and van der Vlugt (31) indicated that cathodic depolarization is involved in anaerobic corrosion. Wormwell and Farrer, apparently with reference to the concepts of polarized electrodes laid down by Evans (5), Evans and Hoar (7) and Brown and Mears (1), suggested that both cathodic and anodic polarization effects are responsible for this increasing negativity.

A study of single electrode potentials shows that iron electrodes in media inoculated with sulfate-reducing bacteria become more anodic with reference to a standard electrode and that the final solution potential assumes some degree of stability. Such a study does not prove that the electrode will or will not be subject to depolarization by sulfate-reducers if made cathodic to another electrode in a galvanic circuit. If an iron cathode in a culture of sulfate-reducing bacteria were isolated as a separate half-cell and connected through an external circuit to an iron anode in a second compartment, the changes in galvanic current and electrode potentials should be subject to study in a manner similar to that used by Evans (5,6), Evans and Hoar (7), and Brown and Mears (1). Essentially, that has been the experimental method employed in this work.

Using the cell described above and illustrated in Figure 1, changes in galvanic current and electrode potentials were studied by closing the external circuit through a series of known resistances. A comparison of inoculated cells and sterile replicas made it possible to study the effects of bacteria. The same method was applied to a study in which sulfate-reducers were grown in bentonite and a third set of exposures was run to study the effects of saturating sterile bentonitic slurries with sulfide. These procedures are described in greater detail as the experimental work is presented.

APPARATUS

A. Potential and Current Measurements

Potential measurements were made with a Type D Rubicon potentiometer of 10^{-5} volt accuracy and Rubicon galvanometer of 0.0122 microampere sensitivity. The latter instrument was also used in making measurements of galvanic current. In the higher current ranges a calibrated shunt was used in parallel with the instrument resistance. The standard cell was a certified Epply Laboratories cell of 1.0193 volt at 20° C with a negative temperature coefficient of 4.05×10^{-5} volt per C°. The standard cell was mounted in a well which was then suspended in the temperature bath.

B. Resistance Measurements

Resistors used in the external circuits were calibrated using a Brown Electro-Measurement Corp. Model 250-C impedance bridge. The Rubicon galvanometer was used as the null point detector in D.C. resistance measurements. The impedance bridge was also used to measure internal cell resistance. A 1000 cycle A.C. signal was used and the null detector in these measurements was a speaker-amplifier unit.

C. Reference Electrodes

Three 1 N calomel reference electrodes were prepared. Two of these, the primary and secondary standards, were prepared in test tubes of approximately 50 ml volume. The third electrode was made up in 12 mm glass tubing with a 3 mm delivery tip filled with 1 N KCl in 3.5% agar gel. The latter was used as a working electrode and was checked against the primary standard after potentials to 0.1 mv were measured. The primary standard electrode was assumed to be stable when variation in the potential difference between it and

the secondary standard did not exceed 0.05 mv. At this time, the primary electrode was assumed to have a half-cell potential of -0.2302 volt. Potential measurements were all relative to this electrode. Periodic checks between the primary and secondary standard electrodes were made. Reference electrodes remained in the temperature bath when not in use.

D. Temperature Control

Temperature was maintained at 25° ± 0.01° C during the time that polarization data were taken and at 25° ± 0.05° C while potential-time data were taken. A mercury-toluene thermoregulator and a vacuum tube relay were adequate to achieve this control.

E. Air Supply

Air was supplied by Model 1 Thiberg aerators. The air was filtered at the intake side of the aerators and brought to temperature equilibrium by passing through copper tubing coils located in the temperature bath. It was next brought to water vapor equilibrium and washed by bubbling through a flask of distilled water also located in the temperature bath. The final air filtration was accomplished by sterile cotton filters mentioned later. (Step 10, Cell Preparation)

PREPARATIONS

A. Steel Electrodes

S.A.E. 1020 steel electrodes of 12 mm diameter (1.13 cm^2 area) with a shoulder of approximately 2 mm diameter and 0.03 in. in depth, were turned from blanks of 0.09 in. thickness. After separation from the blanks, the electrodes were reversed and chucked by the shoulder. The electrode faces were dressed using a constant lathe speed, a constant cross-feed rate, and a 0.001 in. depth of cut. After all signs of surface film were removed, the electrodes were polished with No. 120 emery cloth. Copper lead wires were soldered on the back of the electrodes and threaded through glass shanks as shown in Figure 1. The electrodes, with the shoulders extending into the open end of the glass shank, were then cemented in place[1]. Immediately before exposure they were again polished, cleaned in concentrated nitric acid, and thoroughly rinsed in distilled water. (See electrode sketches, Figure 6).

B. Aluminum Electrodes

Aluminum 61S - T6 electrodes of 18 mm diameter with a center recess 6 mm in diameter and 0.025 in. in depth were turned from blanks of 0.064 in. thickness. The electrodes were center drilled on the lathe and threaded with a 6-32 tap. The heads of half-inch, 6-32 machine screws were turned down until they could be inserted into 6 mm glass tubing and copper lead wires were soldered to them. The screw and lead wire were threaded into

[1] Electrodes were cemented to glass shanks with the Shell Research and Development Co. cement, EPON VI.

the electrode and a safety nut was threaded on the portion of the screw extending through the electrode. The lead wire was run through a 6 mm glass tubing shank and the electrode was cemented to the shank [1] in such a manner that the tubing extended inside the 6 mm center recess. The area of aluminum electrode exposed was approximately that of the steel electrode (1.13 cm^2). The electrode surface opposite the center recess was masked off with cement. When the cement had hardened, the electrode was chucked by the glass shank and the area next to the shank was dressed on the lathe. The remaining steps are the same as those used in the preparation of steel electrodes. In the assembled cell, the electrodes were oriented horizontally with the exposed areas facing upward. The composition of alloys is given below.

Percentage Composition of Alloys

S. A. E. 1020 Steel (Material No. C15679)

Si	Cu	Cr	S	C	Mn	Ni	P	Fe
0.03	0.08	0.04	0.029	0.21	0.50	0.06	0.011	diff.

The mild steel specimens were in the hot-rolled and pickled condition when received.

Al 61 S - T6 (S - 132766)

Si	Cu	Cr	Mg	Al
0.6	0.25	0.25	1.0	diff.

Al 61 S - T6 was in the solution heat treated and artificially aged condition when received.

C. Cell Preparation

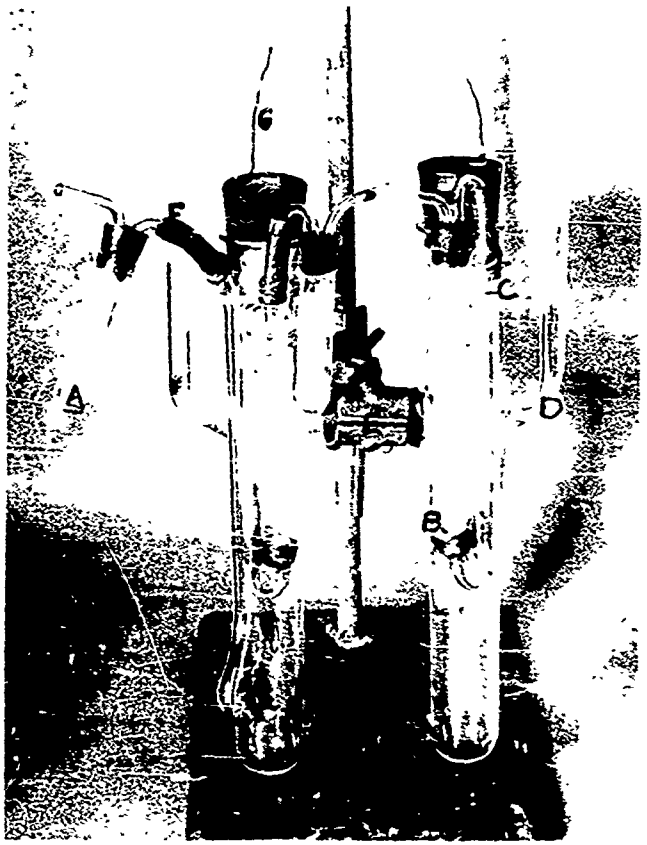
Most of the data presented were taken using the "H" cell shown in Figure 1. This cell was assembled in such a manner that an anaerobic culture of marine sulfate-reducing bacteria in semi-solid nutrient agar filled the lower portion of the right half-cell to a depth of about 3 cm over the face of the electrode. The remainder of the half-cell was filled with 3.5% sea water agar which upon solidification formed a solid bridge through the internal circuit side arm connecting the two half-cells. The left half-cell, which contained sterilized sea water, was provided with aeration tubes. This established the relative oxygen tension in the right and left half-cells. In subsequent discussions, these half-cells will be called respectively, "anaerobic half-cell" and "aerobic half-cell". Sterile controls were run with the inoculated cells and all cells were run in duplicate.

Some data were taken from cells designed to permit variations of the cathode and anode areas. These cells comprised the same circuit as the "H" cells but were composed of two 1500 ml beakers connected by a salt bridge. It was not possible to maintain biological control over these cells and their use was discontinued. The greatest difficulty in obtaining reliable electrochemical data lay in the differences in the internal resistance of the cells.

[1] Electrodes were cemented to glass shanks with the Shell Research and Development Co. cement, EPON VI.

FIGURE I

"H" CELL



This, however, should have little effect on open circuit potentials and these data are presented.

The steps necessary in the preparation of the "H" cells are listed sequentially. Letters in parentheses refer to labels on Figure 1.

1. Filters (A) were filled with cotton, wrapped in paper and sterilized.

2. The side arms and mouth of the aerobic half-cell were plugged with cotton, wrapped in paper, and the unit sterilized empty.

3a. The anaerobic half-cell was prepared in a similar manner except that a short section of rubber tubing, closed on one end by a small cork, was placed on the internal circuit side arm and 40 ml of semi-solid nutrient agar were placed in the half-cell. The unit was then sterilized.

3b. In the experiments in which the electrodes were exposed in saline bentonite, 5 grams of this clay, pretreated [1] with 0.5 liter of nutrient medium, were supported by a pyrex wool pad in the anaerobic half-cell. This procedure was also followed with cells containing sulfide-saturated bentonite. The half-cell was then sterilized.

4. When the nutrient had cooled to a semi-solid state, a 2 ml inoculum of sulfate-reducing bacteria was aseptically introduced deep into the medium. It was found expedient to then incubate the anaerobic half-cell in a Brewer anaerobic jar until blackening of the medium gave evidence of an active culture. In sterile controls step 4 was omitted.

5. The electrode (B) suspended by a glass shank in a No. 5 two hole rubber stopper, was sterilized by dipping in iso-propyl alcohol and drying under ultraviolet light. The electrode was then flamed as it was passed into the half-cell. The second hole of the stopper contained a mercury well.

6. A sterile filter (A) was placed on the vent arm (C) of the anaerobic half-cell and sterile 3.5% agar-sea water was added aseptically through the bridge arm (D).

7. Upon solidification of the 3.5% agar mixture, the internal circuit (E) side arms of both half-cells were unwrapped, flamed, and joined by means of the rubber tubing mentioned in step 5. The cork mentioned in step 3 merely served to contain the agar-sea water mixture before soldification and was removed before joining the two half-cells.

8. The agar sea water mixture was added to the bridge arm of the aerated half-cell. Pyrex wool, placed in the bridge arm before sterilization, supported the agar while still liquid.

9. The cotton plug was removed from the mouth of the aerated half-cell and sterile sea water was added. The electrode was placed in the half-cell using the same procedure as in step 6. Cotton filters were then placed on the aeration tubes.

[1] The method of pretreating bentonite is described in a later section.

10. The cell was placed in a constant temperature bath and the preparation was completed by connecting the affluent aeration tube (F) to a source of washed and filtered air and placing the end of the lead wire (G) of the electrode into the mercury well.

Figure 2 shows the completed cell with an active culture of bacteria in the anaerobic half-cell and the aerator line in place. The external circuit has been closed by placing the leads of a precision resistor into the mercury wells.

Steps 4 through 9 were carried out in a shielded area flooded with ultraviolet light. All sterilization, other than that of the electrode assemblies, was accomplished by autoclaving at 15 psi for 30 minutes.

D. Preparation of Medium

The bacteriological medium used in this work was a modification of that used by Sisler and ZoBell(22) in their studies of hydrogen utilization by marine sulfate-reducers. The composition of the medium is given below.

Bacteriological Peptone	1.00 g
Yeast Extract	1.00 g
Sodium Lactate (60% solution)	4.20 g
$K_2HPO_4.3H_2O$	0.2625 g
$Fe(NH_4)_2(SO_4)_2.6H_2O$	0.3100 g
$MgSO_4.7H_2O$	0.4075 g
Ascorbic Acid	0.0600 g
Agar-agar (Bacteriological)	5.0 g
Sea Water	1 liter

The reagents were weighed out and mixed thoroughly with 1 liter of sea water. The mixture was heated to the boiling point in order to dissolve and disperse the agar-agar, and then poured into the anaerobic cells and sterilized. (Step 3, Cell Preparation). The pH of the medium varied from 6.4 to 6.7, and the redox potential, referred to the standard hydrogen electrode, varied from +225 mv to +195 mv.

E. Preparation of Pretreated Clays

1. Pretreatment of Bentonite for "H" Cell Exposures

Pretreated bentonite was prepared by adding 10 grams of clay to 1 liter of nutrient medium and sterilizing the mixture. The necessity for pretreating is pointed out in the Appendix. Sulfide-saturated bentonite was prepared by bubbling H_2S through the slurry of pretreated bentonite. No agar-agar was included in the nutrient solution used in this procedure and the supernatant liquid was decanted and discarded.

2. Pretreatment of Clays for Beaker Cell Exposures

The effects of sulfide-saturated kaolinite and illite, as well as variously treated bentonitic slurries, were briefly studied in beaker cell exposures. No specific studies, such as those carried out for bentonite (See Appendix) were made to determine the method of pretreating kaolinite and

FIGURE 2
"H" CELL IN OPERATION

FIGURE 3

TEST CELLS IN TEMPERATURE BATH

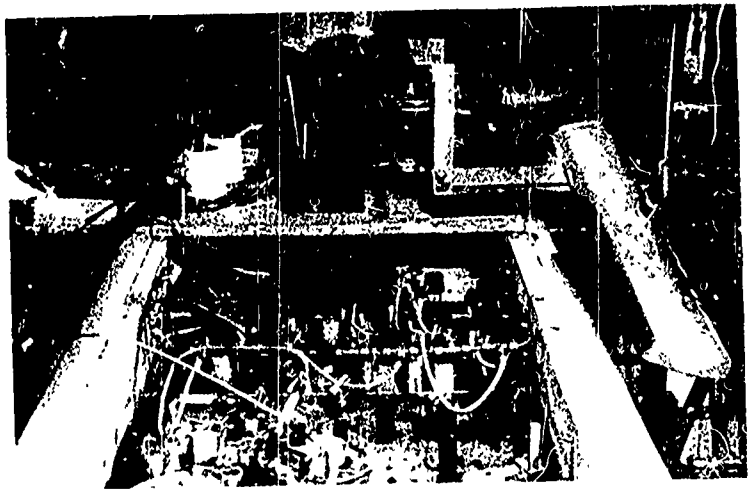
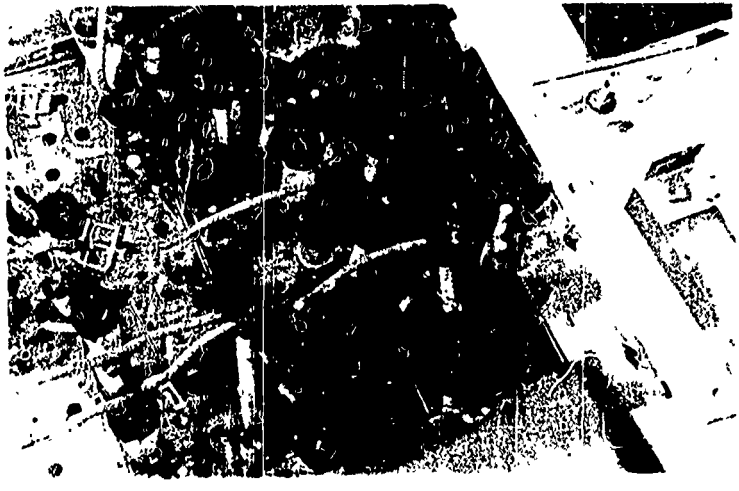


FIGURE 4

"H" CELLS IN TEMPERATURE BATH



illite. The stated amounts of these clays were chosen in order that their volumes, when saturated with nutrient medium, would be approximately equal to the volume of the 20 gram sample of bentonite used in the beaker cell tests.

a. Sulfide-saturated Kaolinite

The clay used in the preparation of the pseudo-sediment was 99.5% pure kaolinite from the Aiken, South Carolina source. Seventy-five grams of the clay were sterilized by dry heat for a period of about 10 hours. The clay was then mixed aseptically with 1 liter of nutrient medium and the slurry was transferred into a 1500 ml half-cell containing a mild steel electrode. After about 18 hours of contact, the supernatant liquid was removed by vacuum and replaced by an equal volume of medium containing 0.35% agar. The slurry was then saturated with H_2S.

b. Sulfide-saturated Illite

The illite used in these preparations was an impure clay containing carbon contaminants. It was, however, practically free of contamination by other alumino-silicate minerals. The pretreatment method was the same as that employed in pretreating kaolinite, except that 200 grams of illite were used.

c. Sulfide-saturated Bentonite

The bentonite used in these experiments was a Harshaw technical grade reagent. The method of preparation was the same as for the two clays mentioned above except that 20 grams of bentonite were used.

d. Sulfide-free Bentonite

Sulfide-free bentonite was prepared in the same manner as other bentonitic pseudo-sediments except that it was not saturated with H_2S.

F. Sea Water

All of the sea water used in this work was taken at one location and time. It was aged according to ZoBell's concepts (40) and chlorinity determinations were made using the Knudsen method (30). The chlorinity was 18.35 °/oo and pH ranged from 8.01 to 8.15. The redox potential (E_h) of the sea water was measured after being in contact with air for several hours. Eh, although unstable, was about 300 mv positive to the standard hydrogen electrode.

G. Inoculations

All inoculations were made with a hydrogen-utilizing, heterotrophic strain (No.354) of Desulfovibrio desulfuricans supplied by the Division of Microbiology of the Scripps Institution of Oceanography.

INTRODUCTION TO EXPERIMENTAL WORK

A. Corrosion Theory

If two metals of different chemical composition are exposed in an electrolyte and connected externally by an electrical conductor, galvanic current flows from one metal to the other. Galvanic current will also flow between two electrodes of identical composition if they are exposed in different electrolytes connected by a salt bridge. Under either of these conditions, the anodic member of the circuit will suffer a loss of weight which is directly related to the galvanic current by Faraday's Law. There are several ways to express Faraday's Law but, from the viewpoint of corrosion electrochemistry, it is most conveniently expressed in terms of weight loss as follows:

$$W_a = \frac{It}{F} Ja$$

where W_a = weight loss of the anode in grams
I = galvanic current in amperes
t = time, in seconds, during which galvanic current flows
F = faraday (96,500 coulombs)
J_a = gram-equivalent weight of anodic metal

In some experiments on galvanic corrosion, it is satisfactory to study weight loss as it is related to galvanic current through Faraday's Law. In other experiments, in which it is impossible to duplicate the natural circuit, investigations may be based upon the change in galvanic current caused by polarization of one or both of the electrodes.

The following resume of corrosion theory, taken essentially from the work of Wesley and Brown (35), should help to explain how such methods are used for different problems in corrosion. In the presentation below potentials are considered as oxidation potentials while the authors mentioned above used the convention of reduction potentials.

The relationship between potentials, current and resistance in galvanic cells may be stated as follows:

$$E_a - E_c = I(R + R_i)$$

where

E_a = polarized potential of the anode
E_c = polarized potential of the cathode
I = galvanic current flow through the cell
R = resistance of the metallic portion of the circuit (external resistance)
R_i = resistance of the electrolytic portion of the circuit (internal resistance)

Emf measurements made with a potentiometer are called open circuit potentials because, at the balance point, opposing voltages are made equal so that no current flows in the circuit being measured. The open circuit potential of the cathode (E'_c) and that of the anode (E'_a) can be related to their polarized potentials by the following expressions:

$$E_c = E'_c + f_c\, I/A_c$$
$$E_a = E'_a - f_a\, I/A_a$$

where f_c and f_a = polarizing functions of the cathode and anode, and A_c and A_a = the areas of the cathode and anode.

Polarization is defined as the change in the potential of an electrode resulting from current flow. Reference to the equations above shows that the potential of the anode changes in the cathodic direction while the potential of the cathode changes in the anodic direction as galvanic current increases. A polarization curve is a curve which illustrates these relationships. It can be visualized that the electrodes of a galvanic circuit cannot continue to polarize indefinitely. If I is plotted against E_c and E_a, the maximum galvanic current is theoretically fixed by the intersection of the cathodic and anodic polarization curves.

In order for the results of corrosion tests to be meaningful, the method of investigation must duplicate natural conditions as nearly as possible. In many corrosion cells, especially those which are produced on a single piece of metal by local differences in the electrolyte, the anodic and cathodic members cannot be separated and recoupled through measuring circuits in a manner comparable to natural conditions. In such situations the study of polarization phenomena can be a very useful method of approach. If E_c and E_a are plotted along the ordinate and galvanic current is plotted along the abscissa, then the vertical distance between points on the anodic and cathodic polarization curves is equal to the drop in potential through the cell. At the point of intersection of the two curves, the cell resistance has theoretically been extrapolated to zero and the maximum galvanic current attainable by such a cell has been reached. Because of this relationship, anodic and cathodic areas, which in nature are separated by extremely small distances, may be isolated as separate half-cells and studied as though they still existed side-by-side.

In neutral or acid electrolytes one of the most common causes of polarization is the electrodeposition of hydrogen upon the cathode. The hydrogen is adsorbed in the atomic state and cannot be evolved unless the cathode potential is equal to or greater than its equilibrium potential plus its hydrogen overvoltage. Adsorbed hydrogen on the metallic surface and hydrogen ion in the electrolyte are the basic components of a gas electrode analogous to the hydrogen electrode. Such an electrode produces an emf in opposition to that of the cell and a consequential decrease in galvanic current. This is essentially the mechanism of cathodic polarization by adsorbed hydrogen.

Sulfate-reducing bacteria are known to be hydrogen-utilizers and it has been suggested that these bacteria more readily utilize atomic hydrogen adsorbed on cathodic surfaces. Such a mechanism is called depolarization and results in greater corrosion rates.

B. Conventions Employed

Throughout the remaining presentation, open circuit potentials are reported as oxidation potentials referred to the standard hydrogen electrode and, when possible, data are presented on duplicate exposures. E_h measurements are also referred to the standard hydrogen electrode. The following

nomenclature will apply throughout the remainder of the paper.

R = external resistance
R_i = internal resistance
P.D. = potential difference between cathode and anode at the time that the external circuit was closed, i.e., cell voltage on open circuit.
IR = potential drop across the resistor in the external circuit.
$I(R + R_i)$ = potential drop through cell.
I = galvanic current
E_a = polarized potential of the anode
E_c = polarized potential of the cathode

C. Exposure Systems

Several electrochemical systems were studied in connection with the corrosion of metals in pseudo-marine environments. The exposure made in beaker cells are outlined in Table 1.

Table 1

Mild Steel Exposures in Beaker Cells

Cell Designation*	Contents of Anaerobic Half-cell	Contents of Aerobic Half-cell
Sulfide-saturated Kaolinite	Slurry of kaolinite in nutrient medium saturated with H_2S	Aerated sea water
Sulfide-saturated Illite	Slurry of illite in nutrient medium saturated with H_2S	Aerated sea water
Sulfide-saturated Bentonite	Slurry of bentonite in nutrient medium saturated with H_2S	Aerated sea water
Sulfide-free Bentonite	Slurry of bentonite in nutrient medium	Aerated sea water
Inoculated Bentonite	Slurry of bentonite inoculated with sulfate-reducing bacteria	Aerated sea water

* In subsequent discussion, the entire cell is considered by reference to the description under "Cell Designation".

In all of the beaker cells, the aerated electrodes were anodic to the air-free electrodes, and in keeping with the terminology applied to the "H" cells, the half-cell containing sterilized sea water has been called the "aerobic half-cell" and the half-cell containing clay has been called the

"anaerobic half-cell". The surface area of all electrodes exposed in the beaker cells was 128 cm^2.

Beaker cells were found objectionable in several ways and a number of exposures were made in the "H" cells previously described. The exposures made in "H" cells are outlined in Table 2.

Table 2

Mild Steel and Al 61 S Exposures in "H" Cells

Cell Designation*	Contents of Anaerobic Half-cell	Contents of Aerobic Half-cell
Mild Steel in Sterile Nutrient Medium	Sterile nutrient medium	Aerated sea water
Mild Steel in Nutrient Medium Inoculated With Sulfate-reducing Bacteria	Nutrient medium inoculated with sulfate-reducing bacteria	Aerated sea water
Mild Steel in Sulfide-free Bentonite	Slurry of bentonite in nutrient medium	Aerated sea water
Mild Steel in Sulfide-saturated Bentonite	Slurry of bentonite in nutrient medium saturated with H_2S	Aerated sea water
Mild Steel in Bentonitic Slurries Inoculated With Sulfate-reducing Bacteria	Slurry of bentonite in nutrient medium inoculated with sulfate-reducers	Aerated sea water
Al 61 S in Inoculated Nutrient Medium	Nutrient medium inoculated with sulfate-reducing bacteria	Aerated sea water
Al 61 S in Sulfide-saturated Bentonite	Slurry of bentonite in nutrient medium saturated with H_2S	Aerated sea water
Al 61 S in Inoculated Bentonite	Slurry of bentonite in nutrient medium inoculated with sulfate-reducers	Aerated sea water
Al 61 S in Sulfide-free Bentonite	Slurry of bentonite in nutrient medium	Aerated sea water

* In subsequent discussion, the entire cell is considered by reference to the description under "Cell Designation".

It should be kept in mind that in all of the cells, the anode and cathode of a given system consisted of the same metal and were prepared in such a manner that they were as nearly identical as possible.

Fifteen hundred ml half-cells were assembled by mounting electrodes and bridges, as well as tubing to permit the addition or withdrawal of solutions, in a paper template which was then fastened over the top of the half-cell by rubber bands. A bubbling stone aerator and an air pressure relief tube were included in the aerated half-cell. Twelve hundred and fifty ml of distilled water were added and the beaker assemblies were autoclaved. Upon removal from the sterilization chamber, hot paraffin (100°C) was poured over the distilled water. After solidification, a second paraffin seal (180° C) was poured which completely filled the space under the paper template. Upon solidification of the paraffin, the distilled water was removed by vacuum and replaced by 1 liter of the appropriate solutions. Upon completion of the half-cell assemblies, the salt bridges of half-cell pairs were connected by a glass "H" tube and filled with 3.5% agar-agar.

PRESENTATION OF DATA OBTAINED USING BEAKER CELLS

A. Corrosion of Mild Steel in Cells Containing Kaolinite and Illite

In spite of the fact that bentonitic clays are often predominant in the sediments of off-shore regions, it was considered advisable to briefly study the relationship between other clay types and galvanic corrosion in the concentration cell produced across the sediment-water interface. Rather than to carry out a complete set of experiments, effects of sulfide-saturated kaolinite and illite are compared with those of sulfide-saturated bentonite.

1. Sulfide-saturated Kaolinite

Duplicate cells were assembled, as previously described, and placed in the temperature bath. Table 3-A contains the chronological changes in oxidation potentials of the mild steel electrodes exposed. After 490 hours, the external circuits were closed through known resistances. Data relating galvanic current to cell resistance are presented in Table 3-B. Data derived from this table are plotted in Figure 5 at the end of the section on beaker cells. Due to variable internal resistance, the galvanic current data from cell 1 are not presented in Table 3-B.

2. Sulfide-saturated Illite

Duplicate cells, similar to those described above for kaolinite, were prepared using illite in the anaerobic half-cell. Table 4-A contains the chronological changes in oxidation potentials of the mild steel electrodes exposed. After 490 hours, the external circuits of the cells were closed through known resistances. The data relating galvanic current to cell resistance are presented in Table 4-B and Figure 5.

Table 3

A. Oxidation Potentials of Mild Steel Electrodes in Aerated Sea Water and H_2S Saturated Kaolinite

Potentials in Volts

Time in Hours	Cell 1		Cell 2	
	Aerobic Half-cell	Anaerobic Half-cell	Aerobic Half-cell	Anaerobic Half-cell
0	+0.466	+0.456	+0.456	+0.452
30	+0.466	+0.458	+0.454	+0.453
54	+0.47[illegible]	+0.457	+0.456	+0.455
74	+0.47[illegible]	+0.457	+0.458	+0.453
90	+0.479	+0.458	+0.458	+0.455
126	+0.481	+0.459	+0.454	+0.454
276	+0.497	+0.461	+0.47[illegible]	+0.458
30[illegible]	+0.499	+0.460	+0.487	+0.458
[illegible]6	+0.511	+0.461	+0.516	+0.459
384	+0.511	+0.462	+0.518	+0.459
490	+0.510	+0.443	+0.516	+0.460

B. Effects of External Resistance on Galvanic Current

Cell I		Cell 2		
R in ohms	I in microamps	R in ohms	I(R + R_i) volts	I in microamps
		5.415×10^5	0.0628	0.110
Data not presented		2.782×10^5	0.0657	0.214
R_i was not constant		5.049×10^4	0.0970	1.22
		5890	0.3405	9.76
		61 90	0.4655	16.0

R_i = 29,000 ohms.
P.D. = 0.056 volt

Table 4

A. Oxidation Potentials of Mild Steel Electrodes in Aerated Sea Water and H_2S Saturated Illite

Potentials in Volts

Time in Hours	Cell 1		Cell 2	
	Aerobic Half-cell	Anaerobic Half-cell	Aerobic Half-cell	Anaerobic Half-cell
0	+0.457	+0.432	+0.453	+0.441
30	+0.456	+0.430	+0.449	+0.442
54	+0.456	+0.428	+0.450	+0.442
74	+0.456	+0.427	+0.451	+0.442
90	+0.457	+0.427	+0.453	+0.443
126	+0.461	+0.424	+0.456	+0.443
275	+0.461	+0.428	+0.461	+0.448
300	+0.461	+0.428	+0.464	+0.449
353	+0.464	+0.431	+0.468	+0.450
384	+0.465	+0.432	+0.468	+0.450
490	+0.475	+0.435	+0.469	+0.452

B. Effects of External Resistance on Galvanic Current

Cell 1			Cell 2		
R in ohms	$I(R + R_1)$	I in microamps	R in ohms	$I(R + R_1)$	I in microamps
6.300×10^5	0.0365	0.061	7.283×10^5	0.0175	0.024
3.185×10^5	0.0780	0.244	3.600×10^5	0.0163	0.045
3.110×10^4	0.0393	1.22	1.436×10^4	0.0194	1.22
3087	0.0326	9.76	170	0.0166	9.76
51	0.0108	9.80	33	0.0154	8.63

R_1 = 1089 ohms
P.D. = 0.038 volt

R_1 = 1560 ohms
P.D. = 0.017 volt

B. Corrosion of Mild Steel in Cells Containing Saline Bentonite

In the present section, cells, comparable to those used in the studies of kaolinite and illite, are described. The cells containing sulfide-saturated and sulfide-free bentonite were intended as controls for systems containing bentonitic slurries inoculated with sulfate-reducing bacteria. Little attention has been given to the study of potential-time data in the present section.

1. Sulfide-saturated Bentonite

Duplicate cells, containing sulfide-saturated bentonite, were prepared in a manner previously described. Table 5-A contains the data on changes in open circuit potentials with time. After 325 hours, the external circuits were closed through known resistances. Data relating galvanic current to cell resistance are presented in Table 5-B and Figure 5.

2. Sulfide-free Bentonite

Duplicate cells were prepared and brought to temperature equilibrium. The external circuits of the cells were left open for a period of only 200 hours as compared to 325 hours in the case of the sulfide-saturated cells. Table 6-A contains the potential-time data which were obtained on these cells. Data relating galvanic current to cell resistance are presented in Table 6-B and Figure 5.

3. Inoculated Bentonite

After the data, from the cells containing sulfide-free bentonite had been taken, the cells were inoculated with a 20 ml inoculum of sulfate-reducing bacteria. The cells were incubated for about 150 hours before further data were taken. During this period, the internal resistance of cell 1 increased to over 170,000 ohms, supposedly due to H_2S gas insulating the tip of the bridge. Changes in external resistance produced little change in galvanic current in this cell and these data are not presented. The internal resistance of cell 2 changed very little and data relating galvanic current to cell resistance are presented in Table 7 and Figure 5. No potential-time data are presented for this period.

The data compiled in part B of Tables 3 through 6 and the data presented in Table 7 have been used to construct curves relating cell resistance to galvanic current. The external resistances (R) were added to the internal cell resistance (R_i) to determine the total cell resistance associated with a measured galvanic current. In Figure 5, log $(R + R_i)$ is plotted against galvanic current. Not all of the points fell along the curves as precisely as those plotted and only enough points are included to indicate the general agreement of results. This was done in order that the five curves might be presented on a single page and thus be more readily compared. None of the data from cell 1, Table 6-B were included in Figure 5 because of high resistance of the cell.

Table 5

A. Oxidation Potentials of Mild Steel Electrodes in Aerated Sea Water and Sulfide-saturated Bentonite

Potentials in Volts

Time in Hours	Cell 1		Cell 2	
	Aerobic Half-cell	Anaerobic Half-cell	Aerobic Half-cell	Anaerobic Half-cell
0	+0.468	+0.440	+0.469	+0.433
250	+0.469	+0.424	+0.477	+0.426
255	+0.466	+0.425	+0.478	+0.426
260	+0.466	+0.425	+0.478	+0.428
275	+0.468	+0.425	+0.477	+0.429
280	+0.460	+0.425	+0.477	+0.431
325	+0.470	+0.426	+0.477	+0.431

B. Effects of External Resistance on Galvanic Current

Cell 1			Cell 2		
R in ohms	$I(R + R_i)$	I in microamps	R in ohms	$I(R + R_i)$	I in microamps
2.504×10^5	.0388	0.153	2.506×10^5	.0634	0.250
1.004×10^5	.1049	1.01	1.000×10^5	.0634	0.616
5.205×10^4	.0706	1.27	5.058×10^4	.0649	1.21
1.596×10^4	.0681	3.49	1.504×10^4	.0662	3.66
2136	.0442	7.75	2112	.0379	7.44
549.6	.0378	9.21	545.5	.0309	8.58
99.61	.0354	9.84	100.7	.0303	9.79
49.79	.0367	10.3	49.99	.0294	9.80
R_i = 3520 ohms P.D. = 0.044 volt			R_i = 3010 ohms P.D. = 0.046 volt		

Table 6

A. Oxidation Potentials of Mild Steel Electrodes in Aerated Sea Water and Sulfide-free Bentonite

Potentials in Volts

Time in Hours	Cell 1		Cell 2	
	Aerobic Half-cell	Anaerobic Half-cell	Aerobic Half-cell	Anaerobic Half-cell
0	+0.469	+0.444	+0.509	+0.449
250	+0.459	+0.443	+0.479	+0.453
255	+0.461	+0.459	+0.480	+0.454
260	+0.461	+0.445	+0.483	+0.452
275	+0.462	+0.444	+0.481	+0.451
280	+0.463	+0.444	+0.481	+0.451

B. Effects of External Resistance on Galvanic Current

Cell 1		Cell 2		
R in ohms	I in microamps	R in ohms	$I(R + R_1)$	I in microamps
5.000×10^5	0.045	5.000×10^5	0.0277	0.055
2.500×10^5	0.085	2.500×10^5	0.0318	0.119
1.000×10^5	0.190	1.000×10^5	0.0304	0.293
1.000×10^4	0.703	1.000×10^4	0.0332	2.44
5000	0.732	5000	0.0312	3.63
1000	0.937	1000	0.307	6.67
500	1.10	500	0.0301	7.34
115	1.12	50	0.0285	7.91
R_1 = 28,500 ohms P.D. = 0.019 volt		R_1 = 3550 ohms P.D. = 0.030 volt		

Table 7

Inoculated Bentonite: Galvanic Current-Cell Resistance Data

Cell 1		Cell 2		
R in ohms	I in microamps	R in ohms	$I(R + R_i)$	I in microamps
		5.018×10^5	0.0207	0.041
Data not presented		2.506×10^5	0.0185	0.073
R_i exceeded 170,000 ohms		1.000×10^5	0.0180	0.174
		5.058×10^4	0.1777	0.329
		1.054×10^4	0.1305	0.939
		2136	0.0178	3.24
		549.6	0.0182	4.55
		100.7	0.0175	5.00
		49.99	0.0175	5.00
		R_i = 3400 ohms		
		P.D. = 0.032 volt		

DISCUSSION OF BEAKER CELL TESTS

It may be argued that the resistance-current relationships presented depend upon the potential differences between the cathodic and anodic electrodes and this, of course, is true. It should be kept in mind, however, that the anodic electrodes were, in every cell, exposed in aerated sea water, and thus the cell variations permit a study of the effects of altering the catholyte. Differences in galvanic current between cells should then, be attributable to differences in catholytes.

With reference to Figure 5, galvanic current below 1.5 microamperes is thought to be primarily controlled by external resistance while current flow in excess of this value is considered to be a function of the polarized potential of the cathode. This concept is supported in the next section where the use of "H" cells lowered internal resistance to less than 300 ohms. The galvanic current produced in these cells was not proportional to this decrease in internal resistance.

Further evidence that the galvanic currents observed were functions of polarized potentials is provided by comparing the internal resistances of the cells. If the galvanic current were primarily controlled by differences in the open circuit potentials of the anode and cathode, then the internal resistance of the cell should limit the galvanic current generated. The highest internal resistance of any of the cells studied occurred in cells containing sulfide-saturated kaolinite. Reference to Figure 5 shows that this cell also produced the highest galvanic current. Similar discrepancies between internal resistance and galvanic current may be noted in the other data presented. There seems to be only a limited relationship between internal cell resistance and galvanic current.

It was thought when the experiments were begun that the open circuit potentials of the duplicate electrodes might have been more nearly equal than they proved to be. These potentials, and thus the potential differences between anode and cathode of duplicate cells, were not reproducible and the interpretation of data given above is subject to some doubt until better duplication is possible.

It may be noted that in the cell in which the catholyte consisted of a bentonitic slurry inoculated with sulfate-reducers, the galvanic current was lower than that of any of the other cells. This tends to contradict the theory that these organisms function as cathodic depolarizers. The measurements were made at a time when the metabolic activity of the culture should have been near its maximum. The decrease in galvanic current can be attributed to neither higher cell resistance nor lower cell voltage since these factors were not greatly changed by inoculating the cell with sulfate-reducing bacteria. Cell voltage (on open circuit) actually increased slightly while internal resistance decreased. Lower galvanic current in the inoculated cell can be explained by assuming that the lower pH of the catholyte after inoculation permitted cathodic polarization. While hydrogen ion might be expected to migrate through the clay slurry the bacteria could not. This would prevent depolarization of the steel cathode. This conclusion is partly borne out by examining the clay sediment after disassembling the cells. It was noted that the clay was only slightly discolored by ferrous sulfide. It is thus assumed that very little physiological activity took place in the clay.

In conclusion, it may be stated that the galvanic current generated by the cells described depends primarily upon the clay type used in the anaerobic half-cell. Effects of neither E_h, pH, nor sulfide, are immediately apparent.

The pH and E_h data on these cells are presented in Table 8. Rather than to inadvertently contaminate the solutions in which the specimens were exposed, the initial pH and E_h values were obtained from small samples prepared for this purpose. The reader is referred to the Appendix for pH and E_h of sulfide-free bentonitic slurries before exposure. The following section on "H" cells also contains more complete data on pH and E_h of cells containing bentonite. Due to the fact that clay deposits were disturbed in disassembling the cells, the final E_h and pH data are not considered entirely representative of conditions at the electrode surface. However, the probes of the measuring electrodes were inserted in the least disturbed part of the clay deposit while making the measurements. It is felt that differences in initial and final pH and E_h in the anaerobic half-cells is a better index of biological contamination than reactions attributable to clays and chemical treatment. E_h and pH will be discussed later in comparison with similar data taken on "H" cells.

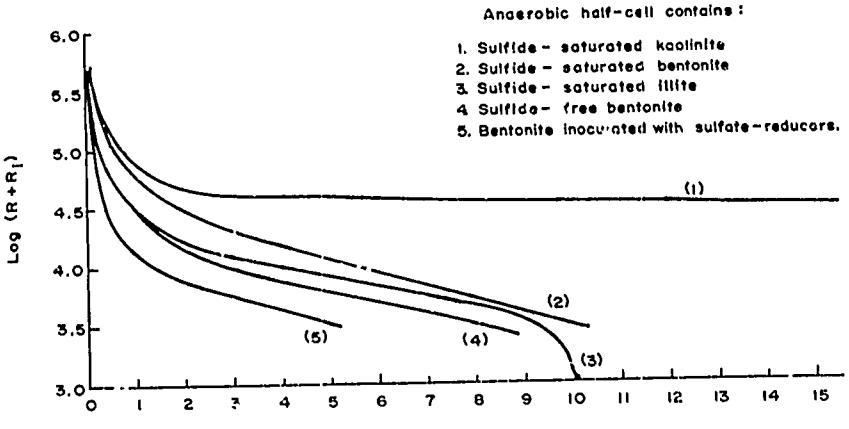
Several factors contributed to the abandonment of beaker cell tests. Among these were high internal resistance, variable internal resistance, the inability to reproduce open circuit potentials of duplicate specimens, and the inability to prevent microbiological contamination. In order to maintain more rigid biological and electrochemical control, the "H" cells were substituted for beaker cells.

Table 8

Beaker Cells: pH and E_h Data

Cell Description	Aerobic Half-cell pH Initial*	pH Final	E_h(mv) Initial	E_h(mv) Final	Anaerobic Half-cell pH Initial*	pH Final	E_h(mv) Initial*	E_h(mv) Final
1-Sulfide-saturated Kaolinite	8.1	7.1	250	+120	5.6	5.7	+65	-10
2-Sulfide-saturated Kaolinite	8.1	7.2	250	+130	—	5.5	—	-40
1-Sulfide-saturated Illite	8.1	7.1	250	+100	5.3	5.7	+135	*25
2-Sulfide-saturated Illite	8.1	7.5	250	+80	—	6.0	—	+5
1-Sulfide-saturated Bentonite	8.1	7.4	250	+120	6.0	6.2	+160	-155
2-Sulfide-saturated Bentonite	8.1	7.4	250	+115	—	6.0	—	-95
1-Inoculated Bentonite	8.1	7.1	250	+115	7.8	7.0	+215	-95
2-Inoculated Bentonite	8.1	7.1	250	+100	—	7.3	—	-75

* Data taken on auxiliary samples prepared for this purpose



BEAKER CELL TESTS: GALVANIC CURRENT VS. TOTAL CELL RESISTANCE.

FIG. 5

"H" CELL EXPERIMENTS

A. Differences Between Beaker Cell and "H" Cell Techniques

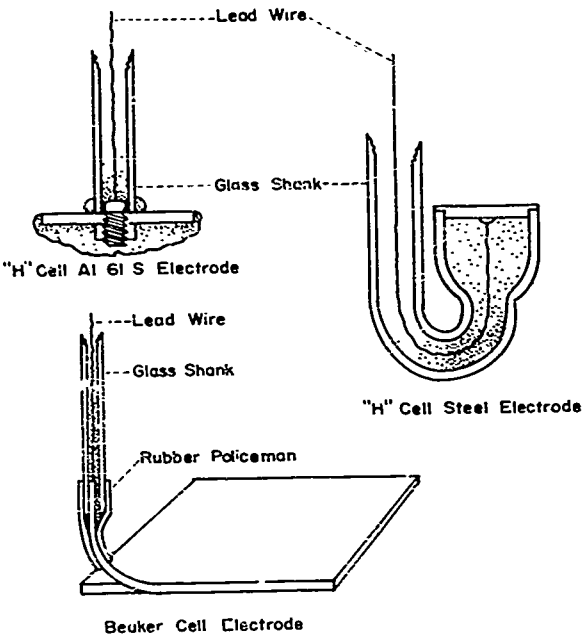
Sketches in Figure 6 show the differences in the three types of electrodes used in the experimental work. (See also Preparation of Electrodes) De Khotinsky cement was used in the construction of the beaker cell electrodes while EPON VI was used in the preparation of "H" cell electrodes. The beaker cell electrodes were sterilized in their respective half-cells by autoclaving in distilled water while the "H" cell electrodes were sterilized by alcohol, ultraviolet light and flaming. In comparison with the "H" cells, the beaker cell aeration was very weak. Only one aerator was placed in each aerated half-cell and its position prevented its being effective in supplying oxygen to the entire electrode. Another variation introduced in the "H" cells was the manner in which the clay was treated. In beaker cell tests the clay was sterilized dry while in the "H" cell tests it was sterilized, after pretreatment, by autoclaving in nutrient medium. This was done to avoid transferring damp clays while trying to maintain sterility. Only minor differences in E_h and pH of clay slurries prepared in the two ways were apparent.

For one or more of the reasons stated above, the polarities of mild steel in the "H" cells were, with two exceptions, opposite to the polarities encountered in the beaker cells. In all of the "H" cell steel exposures made in clays the anaerobic electrode was anodic to the aerated electrode. Only in cells containing sterile and inoculated medium, without clay, were the aerated electrodes anodic to the anaerobic electrodes. Based on the study of potential-time data, it is believed that conditions contributing to the reversal of polarity occurred in both the aerobic and anaerobic half-cells of the "H" cells. The two factors thought to be most important are the use of EPON VI cement and the oxygen concentration of the aerated half-cell.

EPON cement occassionally softened when in contact with aluminum in cells containing sulfides but this was not noted on steel electrodes. No data are presented on aluminum cells in which the cement had softened. Aluminum cells, in general, caused considerable difficulty and the study of aluminum in these cells is quite incomplete. The unfavorable reaction to EPON cement, the development of open circuits in electrode leads and, in several cases, the accumulation of gases within the anaerobic half-cell, resulted in a very limited study of Aluminum 61 S. The reliable data are presented, although duplication was not possible.

B. Experimental Procedure

After the assembled "H" cells had been placed in a temperature bath and brought to 25° C, open circuit potentials of both electrodes were measured with reference to a 1 N calomel electrode. These potentials were recorded chronologically and when relatively stable the external circuit was closed through a known resistance. This resistance was recorded and when the galvanic current through the cell became constant, the IR drop across the resistor was measured and recorded. The physical make-up of the cell and the lack of proper instrumentation made it impossible to determine potentials while the cell was actually drawing current. Instead, the open circuit potential of the more stable electrode in the cell was measured as rapidly as possible.



Stippled Areas Represent Cement.

ELECTRODE SKETCHES

FIG. 6

In cells containing mild steel, the potential of the anode was measured and in aluminum cells, the potential of the cathode was measured. After the first two measurements, the slope of the potential-current curve was estimated and the potentiometer dial set at approximately the predicted potential. Using a system of knife blade switches, the external circuit of the galvanic cell was broken and the potentiometer circuit closed immediately. The galvanometer deflection was noted and the external circuit was restored. The potentiometer dial was moved in the indicated direction of the balance point and after waiting several minutes the measurement was made again. This was repeated until there was perceptible time lag in the galvanometer deflection upon closing the potentiometer circuit. The reference electrode was polarized in these measurements and was consequently checked against the primary standard. Appropriate corrections were made in the polarized potential recorded for the corrosion specimen. The potential of the second electrode was calculated as in the sample calculations below. After the estimation of polarized potentials had been made, the galvanic current of the cell was measured with the Rubicon galvanometer in order to check the previously determined value. The resistance in the external circuit was then decreased and the procedure repeated.

Although the inaccuracy in this method of potential measurements is realized, the data were used, when possible, in the preparation of approximated polarization curves. The limiting currents reported are probably not very accurate but the fact that so crude a method can yield even approximate results, indicates that a better method is available for evaluating biophysical systems in corrosion than has previously been used.

Neither data on mild steel in cells containing sterile medium, nor any of the Al 61 S data could be plotted as polarization curves. The data on these systems are presented as curves relating galvanic current to cell resistance.

In order to prevent confusion concerning the experimental method employed, the following sample calculations are presented.

Assume that a precision resistor of 2112 ohms is placed in the external circuit of an "H" cell, the anaerobic half-cell of which contains a bentonitic slurry inoculated with sulfate-reducing bacteria. Assume also that identical mild steel electrodes are exposed in both half-cells. The external resistance is recorded and the measured drop in potential across this resistor proves to be 0.00691 volt. From Ohm's Law:

$$I = E/R$$

Substituting identities:

$$I = IR/R$$
$$I = 0.00691/2112 = 3.272 \text{ microamperes}$$

The polarized potential of the anode, with reference to the working standard electrode is 0.7134 volt and the difference in potential between the working electrode and the primary standard is 0.0004 volt with the working standard positive to the primary standard electrode. The primary standard electrode

is assumed to have a half-cell potential of -0.2802 volt with respect to the standard hydrogen electrode at 25° C. The corrected polarized potential of the anode is:

$0.7134 + 0.0004 - 0.2802 = 0.4336$ volt (referred to the hydrogen electrode).

At the end of the entire series of measurements made on the cell in question, the internal resistance (R_i) is measured and is found to equal 157 ohms. The total cell resistance is equal to $R + R_i$.

$$R + R_i = 2112 + 157 = 2269 \text{ ohms}$$

While the potential drop across the external resistance is measured directly, the potential drop through the entire cell is equal to the product of galvanic current and total cell resistance.

$$I (R + R_i) = 3.272 \times 10^{-6} \text{ amperes} \times 2269 \text{ ohms}$$

$$= 0.0074 \text{ volt}$$

The polarized potential of the cathode is calculated by the equation:

$$E_a - E_c = I (R + R_i)$$

$$0.4336 \text{ volt} - E_c = 0.0074 \text{ volt}$$

$$E_c = 0.4262 \text{ volt}$$

Oxidation potentials are referred to the standard hydrogen electrode at 25° C. In the "H" cell exposures, the cells are identified by reference to the anaerobic half-cell.

C. Presentation of Data Obtained Using "H" Cells

1. Mild Steel and Al 61 S Exposures in Saline Bentonite

a. Mild Steel in Sterile Nutrient Medium

Duplicate "H" cells, containing mild steel electrodes, were prepared as described under Cell Preparation. In each of the cells, one of the electrodes was exposed in sterile nutrient medium while the other was exposed in aerated sea water. The external circuits were left open for about 220 hours, during which time, open circuit potentials of both specimens were recorded. The external circuits were then closed through known resistances. Potential-time data are presented in Table 9 and polarization data are presented in Table 10. No attempt was made to prepare polarization curves for the data in Table 10. Instead, the data are presented as log ($R + R_i$) vs. galvanic current in Figure 7. Discussion of this figure is reserved until after data on cells containing inoculated medium have been presented.

"H" Cell Tests - Mild Steel : Galvanic Current vs. Total Cell Resistance

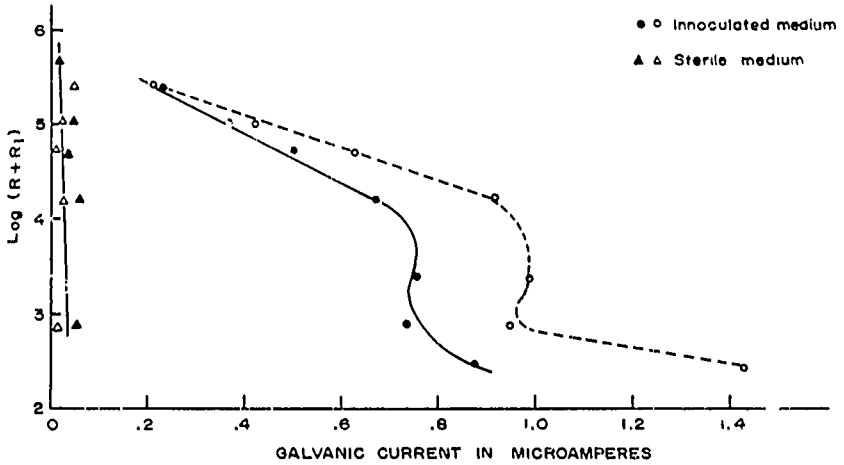


FIG. 7

GALVANIC CURRENT IN MICROAMPERES

FIG. 7

Table 9

Oxidation Potentials of Mild Steel Electrodes in Aerated Sea Water and Sterile Nutrient Medium

Potentials in Volts

Time in Hours	Cell 1		Cell 2	
	Aerobic Half-cell	Anaerobic Half-cell	Aerobic Half-cell	Anaerobic Half-cell
0	+0.426	+0.447	+0.431	+0.452
3	+0.426	+0.448	+0.452	+0.450
6	+0.425	+0.458	+0.430	+0.454
24	+0.417	+0.451	+0.425	+0.453
26	+0.417	+0.452	+0.426	+0.453
155	+0.428	+0.446	+0.455	+0.435
220	+0.445	+0.439	+0.458	+0.436

b. Mild Steel in Nutrient Medium Inoculated With Sulfate-Reducing Bacteria

Duplicate "H" cells were prepared in which one mild steel electrode of each cell was exposed in inoculated nutrient medium while the other was exposed in aerated sea water. Open circuit potentials were measured periodocally for 220 hours after which the external circuits were closed through known resistances. Potential-time data are presented in Table 11 and polarization data are presented in Table 12. The data in Table 12 were used to prepare the polarization curves in Figure 8.

Table 10

Polarization Data: Mild Steel in Sterile Nutrient Medium

Cell 1

R in Ohms	R + R_i in Ohms	I(R + R_i) in Volts	I in Microamps.	E_a in Volts	E_c in Volts
250,400	250,564	.0050	0.0201	+0.4430	+0.4369
100,000	100,164	.0034	0.0340	+0.4443	+0.4409
52,050	52,214	.0019	0.0365	+0.4438	+0.4419
15,040	15,204	.0009	0.0598	+0.4450	+0.4441
2,112	2,276	.0007	0.0284	+0.4450	+0.4449
549.6	713.6	.00004	0.0564	----	----

R_i = 164 Ohms
P.D. = 6 mv

Cell 2

R in Ohms	R + R_i in Ohms	I(R + R_i) in volts	I in Microamps.	E_a in Volts	E_c in Volts
250,600	250,757	.0141	0.0562	+0.4334	+0.4393
100,400	100,557	.0024	0.0234	+0.4345	+0.4321
50,580	50,737	.0006	0.0127	+0.4365	+0.4359
15,960	16,117	.0004	0.0251	+0.4396	+0.4392
2,136	2,293	.0001	0.0512	+0.4393	+0.4398
549.6	706.6	.00001	0.0183	---	---

R_i = 157 Ohms
P.D. = 20 mv

Table 11

Oxidation Potentials of Mild Steel Electrodes in Aerated Sea Water and Inoculated Nutrient Medium

Potentials in Volts

Time in Hours	Cell 1		Cell 2	
	Aerobic Half-cell	Anaerobic Half-cell	Aerobic Half-cell	Anaerobic Half-cell
0	+0.442	+0.425	+0.432	+0.426
3	+0.440	+0.426	+0.430	+0.428
6	+0.437	+0.427	+0.437	+0.429
24	+0.424	+0.416	+0.415	+0.423
26	+0.425	+0.414	+0.415	+0.422
135	+0.410	+0.425	+0.415	+0.348
220	+0.403	+0.328	+0.413	+0.350

It may be noted, in Table 12, that there was an apparent decrease in galvanic current when the external resistance was lowered from the 2100 ohm level to the 550 ohm level. These points were ignored in the preparation of the polarization curves but are included in Figure 7 where galvanic current has been plotted against cell resistance. Whether this decrease in galvanic current is apparent or real is a matter of conjecture. Based on observations of a similar nature made on other cells, it would seem that the decrease actually occurs. It may be, however, that the experimental method is completely unsatisfactory in low external resistance ranges.

It is interesting to note that the cells containing sulfate-reducing bacteria in nutrient medium are completely under cathodic control, i.e., the galvanic current of the cell depends upon the polarized potential of the cathode. This type of control would be expected if sulfate-reducers were depolarizing the cathode.

Data relating total cell resistance to galvanic current are plotted in Figure 7 with similar data taken on sterile medium cells. It is apparent that the inoculated cells are capable of producing as much as 250 times the galvanic current of the sterile cells. The data on open circuit potentials show that the anaerobic electrodes in the inoculated "H" cells became more cathodic than their counterparts in the sterile cells. Based upon the galvanic current data, as well as the polarization and potential-time data, it seems probable that the strain of sulfate-reducing bacteria used in these experiments is capable of depolarizing a steel cathode.

Table 12

Polarization Data: Mild Steel in Inoculated Nutrient Medium

Cell 1

R in Ohms	R + R_i in Ohms	I(R + R_i) in Volts	I in Microamps.	E_a in Volts	E_c in Volts
250,600	250,785	0.0584	0.2330	+0.4062	+0.3478
100,000	100,185	0.0373	0.3730	+0.4068	+0.3694
52,050	52,235	0.0260	0.49762	+0.4072	+0.3812
15,040	15,225	0.0103	0.6782	+0.4076	+0.3974
2,112	2,297	0.0017	0.7576	+0.4079	+0.4062
549.6	734.6	0.0005	0.7320	+0.4073	+0.4068
99.61	284.6	0.00025	0.8760	+0.4076	+0.4073

R_i = 185 Ohms
P.D. = 75 mv

Cell 2

R in Ohms	R + R_i in Ohms	I(R + R_i) in Volts	I in Micrcamps.	E_a in Volts	E_c in Volts
250,600	250,779	0.0524	0.2091	+0.4119	+0.3595
100,400	100,579	0.0426	0.4233	+0.4135	+0.3710
50,580	50,759	0.0321	0.6327	+0.4133	+0.3813
15,960	16,139	0.0149	0.9211	+0.4130	+0.3983
2,135	2,315	0.0023	0.9811	+0.4138	+0.4116
545.5	724.5	0.0007	0.9533	+0.4124	+0.4119
100.7	279.7	0.0004	1.430	+0.4143	+0.4139

R_i = 179 Ohms
P.D. = 65 mv

POLARIZATION CURVES

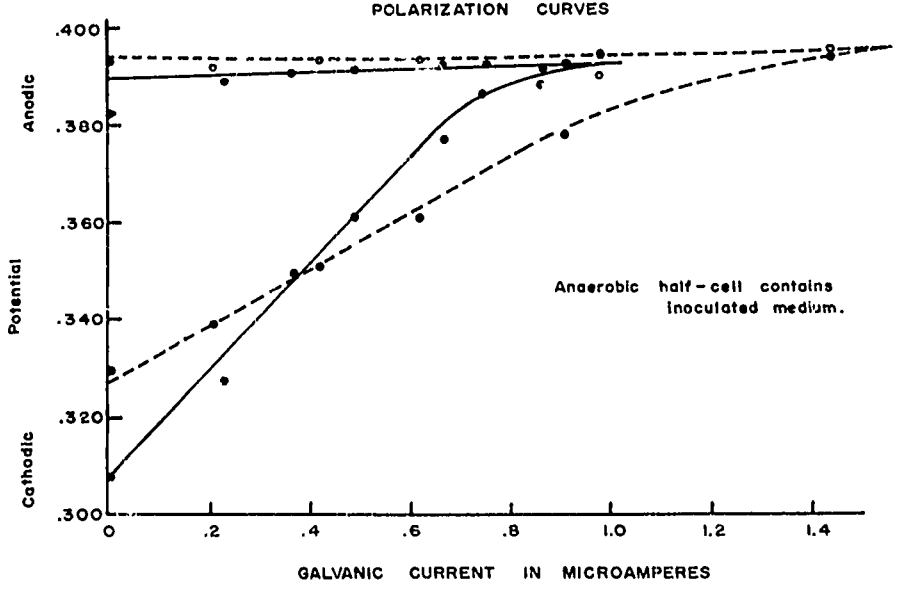


FIG. 8

c. Mild Steel in Sulfide-free Bentonite

Duplicate "H" cells were prepared as described under Cell Preparation. One electrode of each cell was exposed in aerated sea water while the other was exposed in a sterile slurry of bentonite in nutrient medium. Open circuit potentials were recorded and after a period of 166 hours, the external circuits were closed through known resistances. Potential-time data are presented in Table 13 while Table 14 contains polarization data.

The data in Table 14 are presented as polarization curves in Figure 9. The duplication was not good but the curves indicate that the limiting galvanic current would be somewhat less than 3 microamperes. The reason for the difference in P.D., between the two cells, is not immediately apparent.

Table 13

Oxidation Potentials of Mild Steel Electrodes in Aerated Sea Water and Sulfide-free Bentonite

Cell 1			Cell 2		
	Potentials in Volts			Potentials in Volts	
Time in Hours	Aerobic Half-cell	Anaerobic Half-cell	Time in Hours	Aerobic Half-cell	Anaerobic Half-cell
0	+0.418	+0.456	0	+0.440	+0.466
24	+0.420	+0.459	23	+0.442	+0.464
47	+0.437	+0.456	57	+0.435	+0.459
71	+0.423	+0.456	72	+0.438	+0.460
93	+0.425	+0.444	99	+0.442	+0.459
118	+0.426	+0.438	121	+0.445	+0.459
142	+0.427	+0.442	142	+0.448	+0.461
166	+0.425	+0.440	162	+0.448	+0.461

The cells are under mixed control, i.e., the galvanic current depends upon both the polarized potential of the cathode and the polarized potential of the anode. For reasons proposed earlier, the aerated electrode was cathodic to the anaerobic electrode.

d. Mild Steel in Sulfide-saturated Bentonite

Duplicate "H" cells were prepared as previously described. In these cells the anaerotic half-cell contained sulfide-saturated-bentonite.

The method of study was the same as that described under other "H" cell exposures. Potential-time data are presented in Table 15 while Table 16 contains polarization data. In these cells, as in the sulfide-free cells, the aerated electrode was cathodic to the anaerobic electrode. The data in Table 16 were used in the preparation of the polarization curves in Figure 10. The limiting current appears to be slightly greater than 10 microamperes which is higher than any of the other mild steel couples in "H" cells. The cell is almost entirely under anodic control.

e. Mild Steel in Bentonite Slurries Inoculated with Sulfate-reducing Bacteria

Duplicate "H" cells were prepared in which the anaerobic half-cells consisted of a slurry of bentonite in nutrient medium inoculated with sulfate-reducing bacteria. The method of investigation applied to these cells was the same as in previously mentioned exposures in "H" cells. Potential-time data are presented in Table 17. Table 18 contains polarization data from which the polarization curves in Figure 11 were prepared. In these exposures, as in others made in clay, the aerated electrode was cathodic to the anaerobic electrode.

The limiting galvanic current appears to be about 5 microamperes and the cells are under anodic control. These cells were left with external circuits open for a longer period than any of the previously described cells. This was done in order to provide ample time for a change in polarity if it should occur. At the time that the external circuits were closed there was no indication that this might happen.

f. Aluminum 61 S in Inoculated Nutrient Medium

"H" cells containing Al 61 S electrodes were prepard as previously described under Cell Preparation. The cells were so assembled that one electrode was exposed in aerated sea water while the other was exposed in a culture of sulfate-reducing bacteria. Open circuit potentials of both electrodes were measured and recorded periodically. When the open circuit potentials had become relatively stable, the external circuits were closed through known resistances and the galvanic current was measured as cell resistance was decreased. In these cells the aerated electrode was cathodic to the anaerobic electrode, as would be expected with aluminum. Due to the reasons mentioned in the introductory statements in the present section, it was not possible to obtain satisfactory duplication with Al 61 S cells. The data presented on Al 61 S are considered to be the most reliable of those obtained from several cells. No data are presented on Al 61 S in sterile nutrient medium. No attempt was made to prepare polarization curves from data on aluminum cells.

Table 19-A contains potential-time data and data relating galvanic current to cell resistance are presented in Table 19-B. The data in Table 19-B were used to prepare the curve in Figure 12.

Reference to the potential-time data shows that the open circuit potential difference between anode and cathode, at the time the external circuit

Table 14

Polarization Data: Mild Steel in Sulfide-free Bentonite Slurries

Cell 1

R in Ohms	R + R_i in Ohms	I(R + R_i) in Volts	I in Microamps.	E_a in Volts	E_c in Volts
250,600	250,795	0.0139	0.0554	+0.4365	+0.4226
100,000	100,195	0.0126	0.1256	+0.4352	+0.4226
50,580	51,775	0.0113	0.2191	+0.4340	+0.4227
15,960	16,155	0.0074	0.4561	+0.4304	+0.4230
2,136	2,331	0.0022	0.9457	+0.4259	+0.4237
545.5	740.5	0.0008	1.137	+0.4244	+0.4251
99.61	294.61	0.0004	1.205	+0.4244	+0.4240
49.99	244.99	0.0003	1.200	+0.4243	+0.4240

R_i = 195 Ohms
P.D. = 23 mv

Cell 2

R in Ohms	R + R_i in Ohms	I(R + R_i) in Volts	I in Microamps.	E_a in Volts	E_c in Volts
250,400	250,543	0.0194	0.0773	+0.4577	+0.4383
100,400	100,543	0.0158	0.1576	+0.4556	+0.4398
50,580	50,723	0.0140	0.2764	+0.4546	+0.4406
10,540	15,183	0.0167	1.103	+0.4530	+0.4413
2,112	2,255	0.0040	1.799	+0.4472	+0.4432
549.6	692.6	0.0016	2.311	+0.4466	+0.4450
100.7	243.7	0.0006	2.383	+0.4469	+0.4464

R_i = 143 Ohms
P.D. = 22 mv

POLARIZATION CURVES

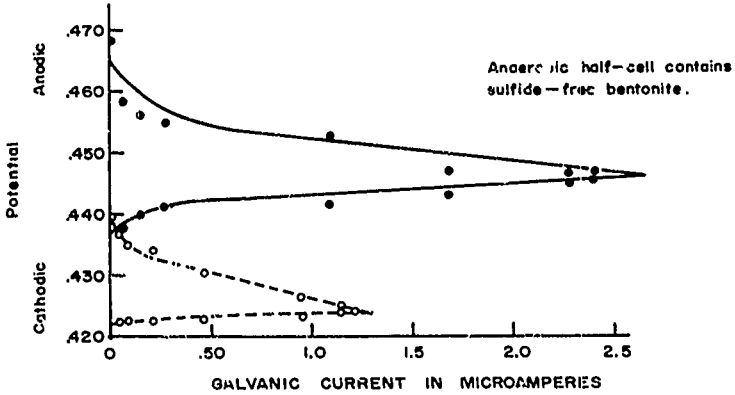


FIG. 9

Table 15

Oxidation Potentials of Mild Steel Electrodes in Aerated Sea Water and Sulfide-saturated Bentonite

Potentials in Volts

Time in Hours	Cell 1		Cell 2	
	Aerobic Half-cell	Anaerobic Half-cell	Aerobic Half-cell	Anaerotic Half-cell
0	+0.409	+0.449	+0.408	+0.457
24	+0.408	---	+0.389	+0.457
47	---	---	+0.377	+0.457
71	+0.437	+0.438	+0.392	+0.456
93	+0.428	+0.460	+0.395	+0.460
118	+0.419	+0.461	+0.398	+0.460
142	+0.413	+0.459	+0.403	+0.462
166	+0.413	+0.455	+0.402	+0.459

was closed (P.D.), was 165 mv. Although the internal resistance of the cell was only 220 ohms, the highest galvanic current measured was only 0.09 microampere and this decreased with a decrease in external resistance. Comparable cells containing mild steel electrodes produced considerably greater galvanic current with a much lower P.D. Obviously, one or both of the electrodes in this cell must have been almost completely polarized. Since aluminum ordinarily polarizes anodically with the formation of aluminum oxide and the anode in this cell was exposed in an oxygen-free electrolyte, it would be of interest to know just what caused the severe current limitation in the cell. Polarization curves would have told much about this mechanism had it been possible to prepare them. However, based on the way in which the anode responded to attempts to estimate its polarized potential, it is believed that most of the polarization of the cell occurred at this electrode.

g. Aluminum 61 S in Sulfide-saturated Bentonite

"H" cells were prepared for this experiment in the manner previously described. Again data on only one exposure are considered accurate. Open circuit potentials of the aluminum electrodes were measured and recorded. After a period of 166 hours the external circuit was closed through known resistances and data relating galvanic current to cell resistance were obtained. The aerated electrode was cathodic to the anaerobic electrode. Potential-time data are presented in Table 20-A and galvanic

Table 16

Polarization Data: Mild Steel in Sulfide-saturated Bentonite Slurries

Cell 1

R in Ohms	R + R_1 in Ohms	I(R + R_1) in Volts	I in Microamps.	E_a in Volts	E_c in Volts
250,400	250,615	0.0420	0.1676	+0.4560	+0.4140
100,000	100,215	0.0388	0.3869	+0.4534	+0.4146
50,580	50,795	0.0349	0.6870	+0.4503	+0.4154
15,040	15,255	0.0253	1.656	+0.4419	+0.4166
2,112	2,327	0.0095	4.067	+0.4284	+0.4189
549.6	746.6	0.0039	5.240	+0.4226	+0.4126
100.7	315.7	0.0018	5.561	+0.4195	+0.4177
49.79	264.79	0.0019	7.230	+0.4163	+0.4144

R_1 = 215 Ohms
P.D. = 42 mv

Cell 2

R in Ohms	R + R_1 in Ohms	I(R + R_1) in Volts	I in Microamps.	E_a in Volts	E_c in Volts
250,600	250,790	0.0537	0.2141	+0.4567	+0.4030
100,400	100,590	0.0497	0.4936	+0.4535	+0.4038
52,050	52,240	0.0449	0.8588	+0.4493	+0.4044
15,960	16,150	0.0315	2.076	+0.4397	+0.4062
2,136	2,326	0.0130	5.571	+0.4210	+0.4080
545.5	737.5	0.0054	7.388	+0.4158	+0.4104
99.61	289.61	0.0024	8.132	+0.4154	+0.4130
49.99	239.99	0.022	9.202	+0.4065	+0.4043

R_1 = 190 Ohms
P.D. = 57 mv

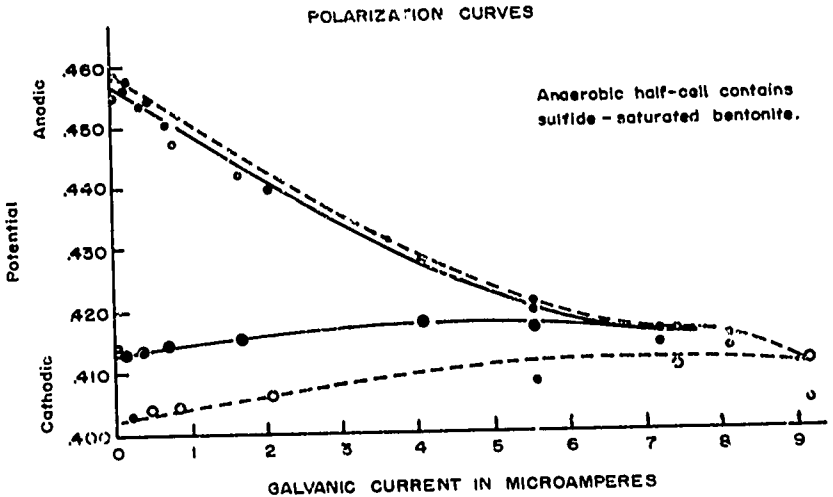

POLARIZATION CURVES
Anaerobic half-cell contains sulfide - saturated bentonite.
Potential
Anodic
Cathodic
.460
.450
.440
.430
.420
.410
.400
0
1
2
3
4
5
6
7
8
9
GALVANIC CURRENT IN MICROAMPERES

FIG. 10

FIG. 10

Table 17

Oxidation Potentials of Mild Steel Electrodes in Aerated Sea Water and Bentonitic Slurries Inoculated with Sulfate-reducing Bacteria

Potentials in Volts

Time in Hours	Cell 1		Cell 2	
	Aerobic Half-cell	Anaerobic Half-cell	Aerobic Half-cell	Anaerobic Half-cell
0	+0.438	+0.453	+0.436	+0.450
23	+0.444	+0.453	+0.439	+0.450
57	+0.442	+0.453	+0.434	+0.451
72	+0.442	+0.455	+0.434	+0.452
99	+0.440	+0.454	+0.430	+0.451
121	+0.435	+0.455	+0.435	+0.452
142	+0.442	+0.455	+0.435	+0.451
162	+0.447	+0.457	+0.436	+0.452
240	+0.442	+0.458	+0.435	+0.452
259	+0.439	+0.455	+0.431	+0.449
286	+0.436	+0.455	+0.431	+0.448
311	+0.436	+0.458	+0.434	+0.451
335	+0.432	+0.457	+0.435	+0.450

current-cell resistance data are presented in Table 20-B. The data from Table 20-P were used to prepare the current-resistance curve in Figure 12. In general, the response of this cell was similar to the cell containing inoculated nutrient medium. Although the P.D. was 70 mv and internal resistance was only 300 ohms, the galvanic current was never any greater than 0.19 microamperes. Again this seemed to be due to anodic polarization.

h. Aluminum 61 S in Inoculated Bentonite

"H" cells containing sterilized sea water in the aerobic half-cell and an inoculated slurry of bentonite and nutrient medium in the anaerobic half-cell, were prepared. Of these cells, only one yielded reliable data. The polarity of the cell was the same as in the other Al 61 S exposures. The method of investigation has been described previously. The external circuit was left open for a longer period than the other aluminum cells in order to observe any latent effects of sulfate-reducers.

Table 18

Polarization Data: Mild Steel in Inoculated Bentonitic Slurries

Cell 1

R in Ohms	R + R_i in Ohms	I(R + R_i) in Volts	I in Microamps.	E_a in Volts	E_c in Volts
250,600	250,757	0.0271	0.1079	+0.4558	+0.4287
100,400	100,557	0.0258	0.2565	+0.4529	+0.4271
52,050	52,207	0.0237	0.4532	+0.4505	+0.4268
15,960	16,117	0.0181	1.120	+0.4453	+0.4272
2,112	2,269	0.0074	3.272	+0.4336	+0.4262
545.5	702.5	0.0030	4.290	+0.4296	+0.4266
99.61	256.61	0.0012	4.618	+0.4260	+0.4248

R_i = 157 Ohms
P.D. = 20 mv

Cell 2

R in Ohms	R + R_i in Ohms	I(R + R_i) in Volts	I in Microamps.	E_a in Volts	E_c in Volts
250,600	250,562	0.0216	0.0861	+0.4464	+0.4198
100,000	100,162	0.0159	0.1590	+0.4462	+0.4263
50,580	50,742	0.0207	0.4079	+0.4441	+0.4234
15,960	16,122	0.0184	1.143	+0.4391	+0.4207
2,112	2,274	0.0068	2.997	+0.4314	+0.4240
545.5	707.5	0.0029	4.143	+0.4273	+0.4244
99.61	261.61	0.0012	4.417	+0.4223	+0.4211

R_i = 157 Ohms
P.D. = 20 mv

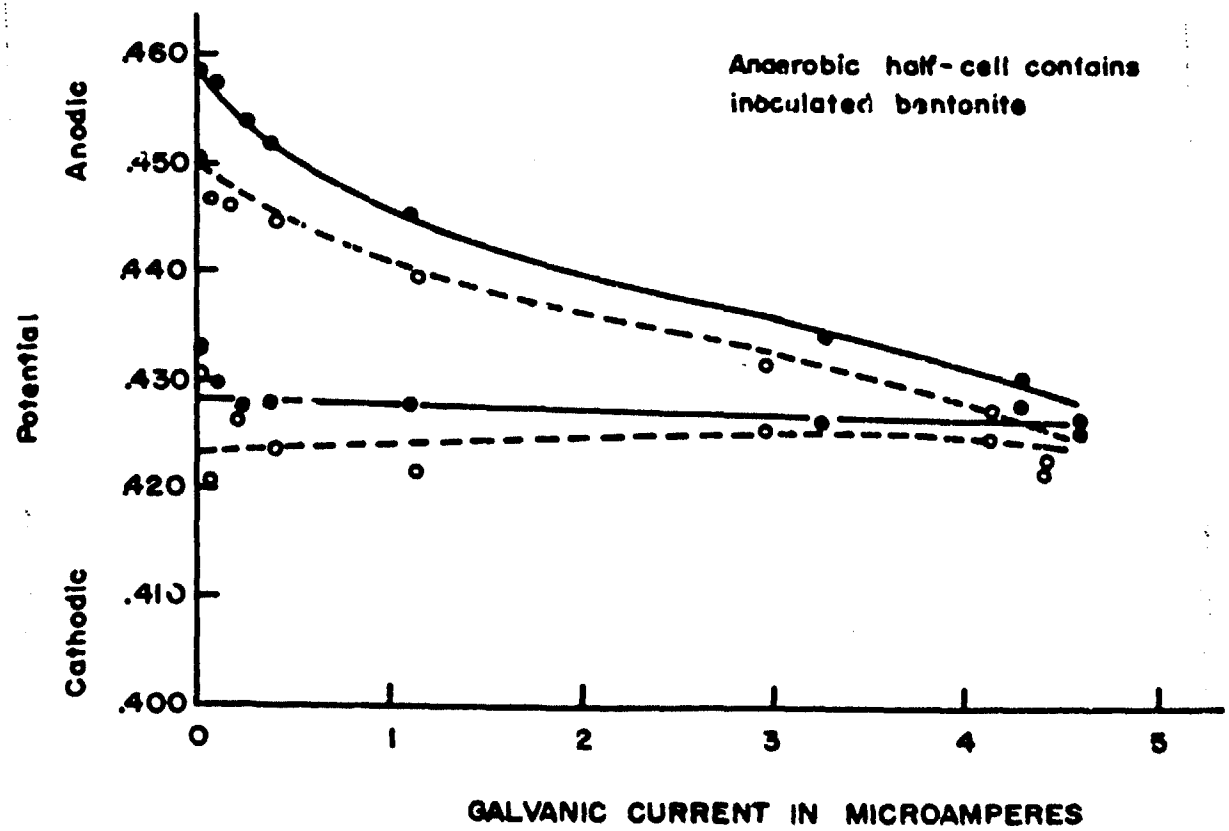

Anaerobic half-cell contains inoculated bentonite
Anodic
Cathodic
Potential
.460
.450
.440
.430
.420
.410
.400
0
1
2
3
4
5
GALVANIC CURRENT IN MICROAMPERES

FIG. 11

Table 19

A. Oxidation Potentials of Al 61 S Electrodes in Aerated Sea Water and Inoculated Nutrient Medium

Time in Hours	Potentials in Volts: Aerobic Half-cell	Anaerobic Half-cell
0	+0.499	+0.634
24	+0.499	+0.639
47	+0.501	+0.646
71	+0.504	+0.655
93	+0.511	+0.663
118	+0.520	+0.678
142	+0.512	+0.669
166	+0.498	+0.663

B. Effects of Cell Resistance on Galvanic Current

R in Ohms	I(R + R_1) in Volts	I in Microamps.	R + R_1 in Ohms
250,400	0.0231	0.0921	250,620
100,400	0.0092	0.0194	100,620
52,050	0.0035	0.0669	52,270
15,040	0.0010	0.0672	15,260
2,112	0.0001	0.0568	2,332
549.6	0.00007	0.0910	769.6

R_1 = 220 Ohms
P.D. = 165 mv

Table 20

A. Oxidation Potentials of Al 61 S Electrodes in Aerated Sea Water and Sulfide-saturated Bentonite

Time in Hours	Potentials in Volts: Aerobic Half-cell	Anaerobic Half-cell
0	+0.493	+0.489
24	+0.499	+0.549
47	+0.503	+0.628
71	+0.508	+0.620
93	+0.496	+0.612
118	+0.498	+0.597
142	+0.505	+0.583
166	+0.506	+0.576

B. Effects of Cell Resistance on Galvanic Current

R in Ohms	I(R + R_i) in Volts	I in Microamps.	R + R_i in Ohms
250,400	0.0426	0.1699	250,600
100,000	0.0182	0.1820	100,200
52,050	0.0091	0.1741	52,250
15,960	0.0023	0.1422	16,160
2,112	0.00027	0.1184	2,312
549.6	0.00007	0.0910	749.6

R_i = 200 Ohms
P.D. = 72 mv

40-a

'H" Cell Tests - Al 61 S: Galvanic Current vs. Total Cell Resistance

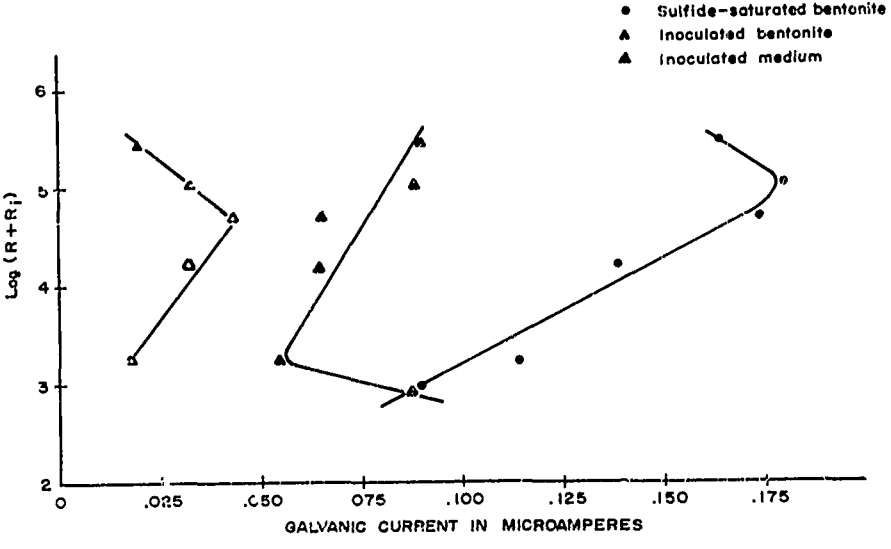


FIG. 12

Table 21-A contains potential-time data taken on this cell. Galvanic current and resistance data are presented in Table 21-B. The data from Table 21-B were used to prepare the current-resistance curve in Figure 12. The results recorded are very similar to those of previous "H" cell tests of Al 61 S. The galvanic current was extremely low and decreased with decreasing external resistance. The cell seemed to be anodically polarized.

In the three experiments on aluminum described above, it should be noted that all of the cells contained high concentrations of sulfides and that galvanic current was very low. In the experiment described below, the anaerobic half-cell contained sulfide-free bentonite. The galvanic current produced by this cell was higher than in any of the other aluminum cells. Since sulfides are generally corrosive to aluminum, it is difficult to explain these contradictory current-resistance relationships.

1. Aluminum 61 S in Sulfide-free Bentonite

Data are presented in Table 22-A and Table 22-B for tests in which the anaerobic electrode was exposed in a sulfide-free bentonitic slurry. Again the aerated electrode was cathodic to the anaerobic electrode. The experimental procedure was the same as in other "H" cell tests. Reference to the potential-time data shows that the open circuit potential of the anode was almost 250 mv greater than that of the cathode when the circuit was closed. This high P.D. is reflected in the galvanic current which is about 10 times as great as any of the cells containing sulfide. Why this should have occurred is not at all clear since sulfides are generally anodic stimulators. The relationship between galvanic current and cell resistance is plotted in Figure 13.

2. Discussion of E_h and pH Data

E_h and pH data, taken on "H" cell exposures, are presented in Table 23. The cells are identified by reference to the anaerobic half-cell. Except for the final pH and initial E_h values of the aerobic half-cells and the final E_h values of the anaerobic half-cells, the "H" cell data are in general agreement with the beaker cell data in Table 8.

Due to instability, E_h measurements were difficult to make. The one exception to this statement occurred with anaerobic systems containing sulfate-reducing bacteria. Saturating a bentonitic slurry with H_2S did not lower E_h to values comparable to those encountered in active cultures of bacteria. It may also be noted that redox potentials in inoculated bentonite were not as low as those in inoculated medium.

In the beaker cell tests, low E_h may have been partly responsible for the anaerobic electrode being cathodic to the aerobic electrode. As mentioned before, the low E_h values noted in the beaker cell tests were probably due to microbiological contamination. In the "H" cell tests, rigid bacteriological controls were applied and no data are presented from cells which were biologically contaminated. In the latter cells, low redox potentials were encountered only in anaerobic half-cells containing no clay. In such cells, the anaerobic electrode was cathodic to the aerobic electrode.

Table 21

A. Oxidation Potentials of Al 61 S Electrodes in Aerated Sea Water and Inoculated Bentonite

Time in Hours	Potentials in Volts: Aerobic Half-cell	Anaerobic Half-cell
0	+0.498	+0.654
57	+0.501	+0.624
72	+0.502	+0.622
121	+0.501	+0.617
162	+0.499	+0.617
240	+0.502	+0.587
286	+0.499	+0.561
311	+0.499	+0.551
335	+0.493	+0.542

B. Effects of Cell Resistance on Galvanic Current

R in Ohms	$I(R + R_1)$ in Volts	I in Microamps.	$R + R_1$ in Ohms
250,600	0.0052	0.0206	250,900
100,400	0.0033	0.0326	100,700
52,050	0.0025	0.0469	52,340
15,040	0.00055	0.0359	15,340
2,136	0.00005	0.0187	2,436

R_1 = 300 Ohms
P.D. = 50 mv

Table 22

A. Oxidation Potentials of Al 61 S Electrodes in Aerated Sea Water and Sulfide-free Bentonite

Time in Hours	Potentials in Volts: Aerobic Half-cell	Anaerobic Half-cell
0	+0.488	+0.884
57	+0.504	+0.747
72	+0.502	+0.828
121	+0.502	+0.795
162	+0.506	+0.793
240	+0.506	+0.793
286	+0.507	+0.702
311	+0.511	+0.704
335	+0.514	+0.755

B. Effects of Cell Resistance on Galvanic Current

R in Ohms	$I(R + R_i)$ in Volts	I in Microamps.	$R + R_i$ in Ohms
250,600	0.2010	0.8015	250,790
100,000	0.0997	0.9950	100,190
52,050	0.0748	1.432	52,240
15,960	0.0272	1.687	16,150
2,136	0.0040	1.732	2,326
547.5	0.0013	1.742	735.5
100.7	0.00054	1.854	290.7

R_i = 190 Ohms
P.D. = 250 mv

"H" Cell Tests – Al 61 S: Galvanic Current vs. Total Cell Resistance

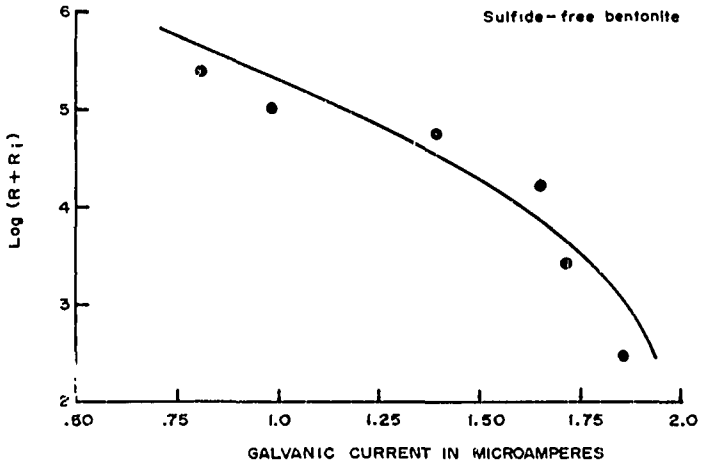


FIG. 13

Table 23

"H" cells: pH and E_h Data

Cell Description	Aerobic Half-cell				Anaerobic Half-cell			
	pH		E_h (mv)		pH		E_h (mv)	
Mild Steel in:	Initial*	Final	Initial*	Final	Initial*	Final	Initial*	Final
1-Sterile Medium	8.1	7.7	+170	+140	6.6	6.1	+205	-150
2-Sterile Medium	8.1	7.7	+170	+200	6.6	6.0	+205	-130
1-Inoculated Medium	8.1	7.8	+170	+165	6.6	6.6	+205	-395
2-Inoculated Medium	8.1	7.7	+170	+160	6.6	6.5	+205	-555
1-Sulfide-free Bentonite	8.2	8.1	+150	+170	6.8	6.5	+230	+80
2-Sulfide-free Bentonite	8.2	8.2	+150	+115	6.8	7.3	+230	+70
1-Sulfide-saturated Bentonite	8.2	8.1	+150	+170	6.7	6.7	+160	+125
2-Sulfide-saturated Bentonite	8.2	8.3	+150	+155	6.7	6.7	+160	+155
1-Inoculated Bentonite	8.1	8.2	+185	+215	6.8	6.6	+240	+85
2-Inoculated Bentonite	8.1	8.2	+185	+210	6.8	6.6	+240	+80
Al 61 S in:								
Inoculated Medium	8.1	8.3	+175	+156	6.6	6.5	+200	-135
Sulfide-saturated Bentonite	8.1	8.2	+160	+144	6.7	7.3	+170	+96
Inoculated Bentonite	8.1	8.4	+160	+100	6.8	6.6	+260	+37
Sulfide-free Bentonite	8.1	8.6	+200	+51	6.8	7.2	+210	+45

* Data taken on auxiliary samples prepared for this purpose

It seems porbable that low E_h has much to do with polarity of the cells described in these experiments.

Table 23 shows that substantially lower pH values were found in the aerobic half-cells of the sterile and inoculated medium exposures than in any of the other aerobic half-cells. The galvanic current is considered rather low to have produced this effect although no other reason is immediately apparent.

A generalized statement concerning possible effects of E_h and pH on corrosion mechanisms in low E_h environments, would probably be of more value than further comment on specific cells. The reader is referred to Mason (15) for a more complete discussion of E_h and pH in natural environments.

E_h is a relative figure referred to the reaction:

$$H_2 = 2H + 2e-$$

In practice, it is the open circuit potential between an inert electrode, such as a platinum wire, and a standard reference electrode. While the half-cell potential of the reference electrode is constant, the half-cell potential of the platinum wire will depend upon the ability of the system being measured to oxidize or reduce another chemical system.

Consider the equation:

$$E = E_o + \frac{RT}{nF} \ln Q$$

and the reaction:

$$H_2 = 2H^+ + 2e^- \qquad (E_o = 0.000)$$

Solving the reaction for Q and substituting into the equation:

$$E = E_o + \frac{RT}{nF} \ln (H^+)$$

where:

E = the half-cell potential of the hydrogen electrode under any condition of temperature, H_2 pressure and hydrogen ion concentration.
E_o = half-cell potential of the standard hydrogen electrode
R = gas content (8.314 joules degree^{-1} mol^{-1})
T = absolute temperature
n = number of electrons involved in the reaction
F = Faraday's number
(H^+) = hydrogen ion concentration

At 25° C the expression simplifies to:

$$E = 0.000 + 0.06 \log (H^+)$$

At pH = 6, log (H^+) = -6 and the expression above becomes:

$$E = -.360 \text{ volt}$$

Thus at a pH of 6 in a system with a redox potential of -360 mv, the hydrogen oxidation reaction, written above, would be in equilibrium. If the E_h were to become slightly more negative, hydrogen gas could theoretically be evolved from any surface at which hydrogen ion could be reduced. This does not occur in nature, however, because of hydrogen overvoltage.

For instance, a greater potential than the theoretical potential is required to break the adsorption bond of atomic hydrogen to steel. At least a part of this required energy could be supplied by the potential difference between the anode and cathode of a galvanic cell similar to those described in these experiments. Thus, if the polarity of the cell favors the reaction, i.e., if the anaerobic electrode is cathodic, then it is possible for cathodic depolarization to occur independently of the metabolic activity of sulfate-reducing bacteria. Actually, the breaks in the galvanic current-cell resistance curves in Figure 7 may be interpreted this way. If the interpretation is correct, the effects of sulfate-reducers would be realized at extremely high external resistances. Corrosion by sulfate-reducing bacteria is usually considered a micro-cell mechanism in which the external resistance would be extremely low. Thus, it is possible that the study of anaerobic microbiological corrosion should actually hinge upon the determination of hydrogen overvoltage under low E_h conditions.

CONCLUSIONS

Although experimental results have been discussed as they were presented, a few general comments may aid in relating these studies to the general field of corrosion experimentation.

The most important single fact that can be established by corrosion tests is the polarity of the galvanic cell under consideration. Beyond this, corrosion testing is semi-quantitative. Although the instruments and techniques applied are inherently capable of yielding precise and accurate results, the inhomogeneity of commercial metals and alloys makes it impossible to reproduce potential and current values. For this reason, corrosion testing belongs in the general category of statistical studies in spite of the fact that the experimental methods employed are based on some of the most precisely known relationships in physical chemistry.

Unless the corrosion test is carried out under conditions identical to those in nature, the results cannot be reliably applied to corrosion engineering. It may be remembered that in the experiments described, the polarities of cells containing mild steel in clays were actually reversed by changing from beaker cell to "H" cell exposures. If these experiments were a part of a complete corrosion investigation, the next phase would be field testing. To the authors knowledge no work has been done on the distribution of relative polarities on metals extending through the mud line in marine environments. The experiments also point out a need for studying electrical conductivity of different clay types in natural sediments. It would also be

advisable to duplicate bottom oxygen concentrations in aerated half-cells if further laboratory studies were made.

While the galvanic current values reported in these experiments may appear to be too low to produce serious corrosion, it should be kept in mind that it is not possible to completely isolate local anodes and cathodes in order to include them in measuring circuits. Polarization curves provide much information on limiting galvanic current but in these experiments the curves are probably least accurate in the region of low cell resistance. There is also to be considered the possible effects of E_h and pH on anaerobic corrosion. A very interesting study could be made by modifying the procedure and repeating parts of this work. Using a cell of extremely low internal resistance and a high frequency electronic interrupter to alternately make galvanic current and potential measurements of corroding electrodes, more realistic results could be obtained than those reported.

In conclusions, three observations are of particular interest. These are:

1. In concentration cells, such as those described in these experiments, it is possible that the cathodic electrode may exist in the oxygen-free environment.

2. [illegible] strain of sulfate-reducing bacteria used in these experiments is apparently capable of depolarizing a steel cathode.

3. With the modifications listed above, the method of investigation employed offers much greater promise of critically evaluating microbiological corrosion mechanisms than other methods currently in use.

APPENDIX

A. Pretreatment of Bentonite

1. Effects of Bentonite on Redox Potential and pH of Sea Water

In the first attempts to grow sulfate-reducers in slurries of bentonite in bacteriological medium, the clay compacted so firmly that it was thought impossible for that organism to grow in it. This was considered to be due to the high concentration of calcium ion in the medium. Calcium ion was replaced with sodium ion and some improvement resulted but bacteria could still not be made to grow readily in the clay. This occasioned a more systematic examination of the effects of bentonite on physico-chemical properties of sea water and the medium employed.

It was considered advisable to attempt to find the volume of sea water necessary to stabilize a given quantity of bentonite with respect to E_h and pH. These factors are important in culturing sulfate-reducers. A pH of 6.4 to 7.0 and a low E_h insure more rapid growth although the use of a Brewer anaerobic jar (Step 5, Cell Preparation) somewhat mitigates the E_h and pH demands made of culture media. It would be beyond the scope of this problem to completely evaluate effects due to bentonite and although the results were not altogether satisfactory, the system described below was employed in determining the volume of sea water required to pretreat bentonite.

Measurable effects of bentonite on either the pH or E_h of sea water should become evident by measuring these factors in a sea water supernatant from which bentonite has settled. In order to test this possibility, various concentrations of bentonite were prepared using sea water filtered through a Seitz filter. The E_h and pH of the supernatant sea water were measured and recorded at the indicated times. E_h[1] was measured at a platinum wire with respect to a saturated calomel electrode and since the factor $D(E_h)$, defined below, is arbitrary, E_h measurements have not been referred to the hydrogen electrode. Immediately after making a measurement, the bentonitic slurry was stirred with a magnetic mixer for several minutes and the clay was permitted to settle from the sea water before the next measurement was made. These values became relatively stable after about 40 hours and the tests were terminated. The data are presented in Table 1-A. The redox potentials are reported in millivolts and the number of significant figures reflects the stability of the system. There was no apparent reason for variable stability but, in general, the more positive potentials showed greater stability.

Since considerable variation occurred in the E_h and pH of the sea water blank, it was necessary to consider how much of the E_h and pH change in the samples was due to reactions with bentonite. The E_h and pH data were plotted against time. The E_h of the sea water blank minus that of each bentonite concentration, was read from points simultaneous in time on these curves and recorded as $D(E_h)$. Values for the pH of the sea water blank minus that of the several samples were recorded as D(pH). Bentonite concentration is considered

[1] The notation, E_h, is usually considered to be referred to the standard hydrogen electrode but, for convenience of presentation, it implies here the open circuit potential between a platinum wire and the saturated calomel electrode.

to be primarily responsible for the magnitudes of $D(E_h)$ and D(pH). These values are plotted against log bentonite concentration in Figure 1-A. The curves are prepared only from data taken after 42 hours of exposure.

Table 1-A

Effects of Bentonite on E_h and pH of Sea Water

Bentonite Concentration	E_h (mv)		pH		Hours of Exposure
	Sample 1	Sample 2	Sample 1	Sample 2	
0 g/l	-25	-25	8.01	8.01	1
" "	+150	+164	8.06	8.09	26
" "	+153	+152	8.16	8.17	32
" "	+37	+37	8.17	8.17	42
" "	+38	+38	----	----	45
0.01 g/l	-6.8	-3.4	8.00	8.01	2
" "	+162	+156	8.08	8.10	26
" "	+130	+134	8.16	8.14	32
" "	+67	+67	8.17	8.16	43
" "	+39	+41	----	----	46
0.1 g/l	+7.3	+18.7	8.02	8.02	2
" "	+156	+155	8.06	8.09	26
" "	+130	+132	8.14	8.15	32
" "	+63	+58	8.16	8.18	43
" "	+95	+57	----	----	48
1.0 g/l	+ 27.7	+13.2	8.02	8.02	3
" "	+70	+75	8.09	8.08	26
" "	+128	+119	8.14	8.14	33
" "	+47	+47	8.15	8.15	43

Table 1-A (cont.)

Effects of Bentonite on E_h and pH of Sea Water

Bentonite Concentration	E_h (mv) Sample 1	E_h (mv) Sample 2	pH Sample 1	pH Sample 2	Hours of Exposure
1.0 g/l	+51	+45	----	----	48
5.0 g/l	+16	+30.2	7.90	7.89	3
" "	+73	+78	8.04	8.04	26
" "	+121	+120	8.08	8.10	33
" "	+46	+46	8.11	8.12	44
" "	+39	+43	----	----	48
10.0 g/l	+31.3	+31.3	7.84	7.86	3
" "	+78	+76	8.00	8.01	26
" "	+102	+102	8.01	8.05	33
" "	+61	+64	8.04	8.04	44
" "	+45	+47	----	----	48
20.0 g/l	+35.7	+34.3	7.74	7.78	4
" "	+87	+88	7.99	8.00	26
" "	+93	+93	7.94	7.98	33
" "	+ 62	+68	7.93	7.96	44
" "	+42	+33	----	----	49

2. Effects of Bentonite on Nutrient Medium

After the last E_h and pH measurements had been made, the supernatant sea water was decanted and replaced with an equal volume of nutrient medium. These mixtures were sterilized and left covered for 36 hours. During this time the clay fraction was resuspended several times by agitation. At the end of the exposure period the beakers were uncovered and measurements of E_h and pH were made. $D(E_h)$ and D(pH) were computed as before. Table 2-A contains these data as the average of two samples. E_h and pH data were also taken at time intervals after the first 36 hours. It soon became evident, however, that the effects being measured were those of biological contamination introduced by the measuring electrodes. In order to prevent introducing

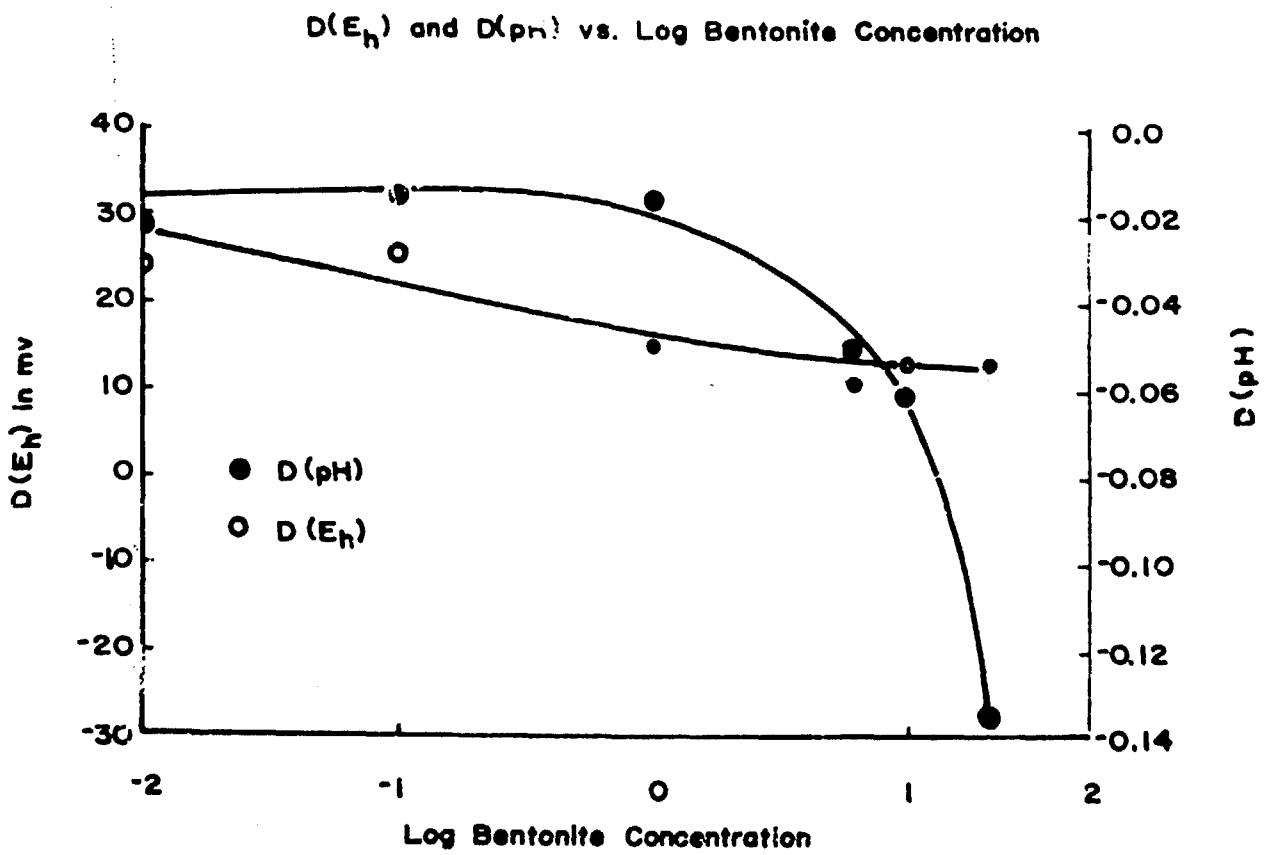

D(Eh) and D(pH) vs. Log Bentonite Concentration
40
30
20
10
0
-10
-20
-30
0.0
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
D(Eh) in mv
D(pH)
● D(pH)
○ D(Eh)
-2
-1
0
1
2
Log Bentonite Concentration

FIG. 1-A

this error, it would have been necessary to maintain sterility until immediately before making any measurement. None of the data on changes in E_h and pH with time are presented.

Table 2-A

Effects of Bentonite on E_h and pH of Nutrient Medium

Bentonite Concentration	pH	E_h(mv)	D(pH)	D(E_h) in mv
0 g/l	6.50	-55	----	----
0.01 g/l	6.92	-70	-0.42	+15
0.1 g/l	6.68	-47	-0.38	-8
1.0 g/l	6.60	-35	+0.02	-20
5.0 g/l	6.66	+15	-0.16	-70
10.0 g/l	6.80	+14	-0.30	-69
20.0 g/l	6.93	+7	-0.43	62

The data plotted in Figure 1-A indicate that concentrations of bentonite in sea water which exceed 1 gram per liter, produce rather marked effects on pH. Apparently the change in E_h, attributable to bentonite, takes place at about 0.1 gram per liter. The data in Table 2-A show that these same concentrations of bentonite are critical with respect to E_h and pH changes in the nutrient medium. The smallest value of D(pH) occurred with a bentonite concentration of 1.0 gram per liter of nutrient medium and the smallest value of D(E_h) occurred with a bentonite concentration of 0.1 gram per liter of nutrient. It may also be noted from Table 2-A that the greatest difference in E_h between any two samples is 70 mv and the greatest difference in pH is 0.43 unit. All values of pH are below 7.0 and the most positive E_h is +14 mv. This would indicate that neither the buffer capacity nor the redox poise of the medium had been greatly exceeded.

During the course of the entire research program, there were some 50 or more exposures made in clay. Due to the lack of a sufficient quantity of aged sea water, it was impossible to pretreat the clay with the volume of sea water shown to be required by the above tests. Assuming 50 exposures of 5 grams of clay per exposure, 2500 liters of aged sea water would have been required for merely stabilizing clay with respect to E_h and pH. Based primarily on the limitations just stated and the data plotted in Figure 1-A, 10 grams of clay per liter of nutrient medium was rather arbitrarily chosen as the pretreatment ratio. On the basis of electrochemical results obtained, this method is not considered adequate although sulfate-reducers can be made to grow in clay which has been sterilized in nutrient medium at a concentration of 10 grams of clay per liter of nutrient.

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